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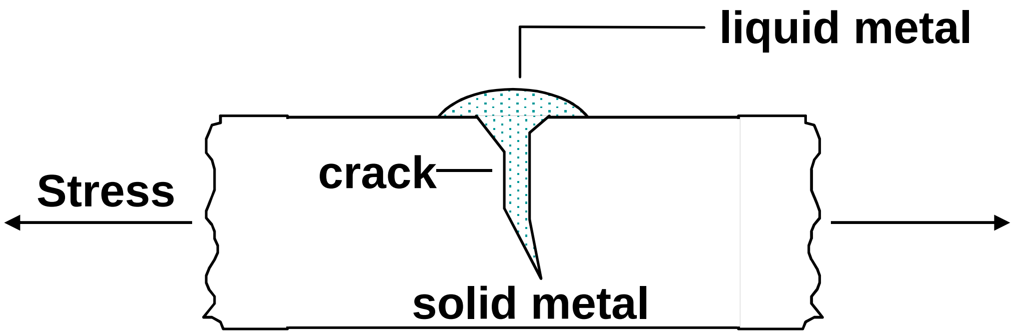
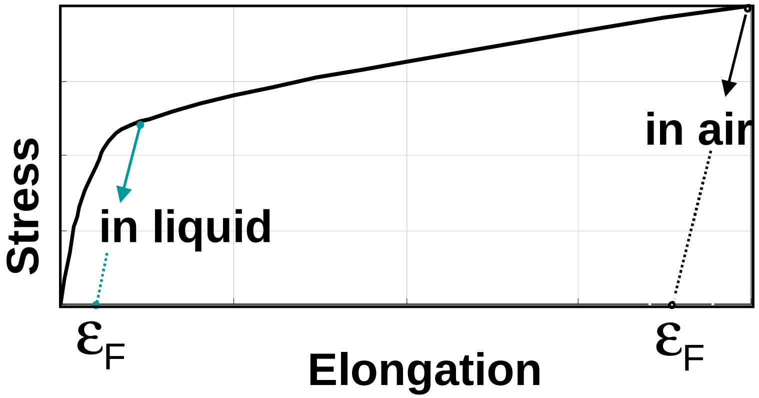
LIQUID METAL EMBRITTLEMENT : driving force , crack kinetics , macroscopic manifestations

LME : What It Looks Like

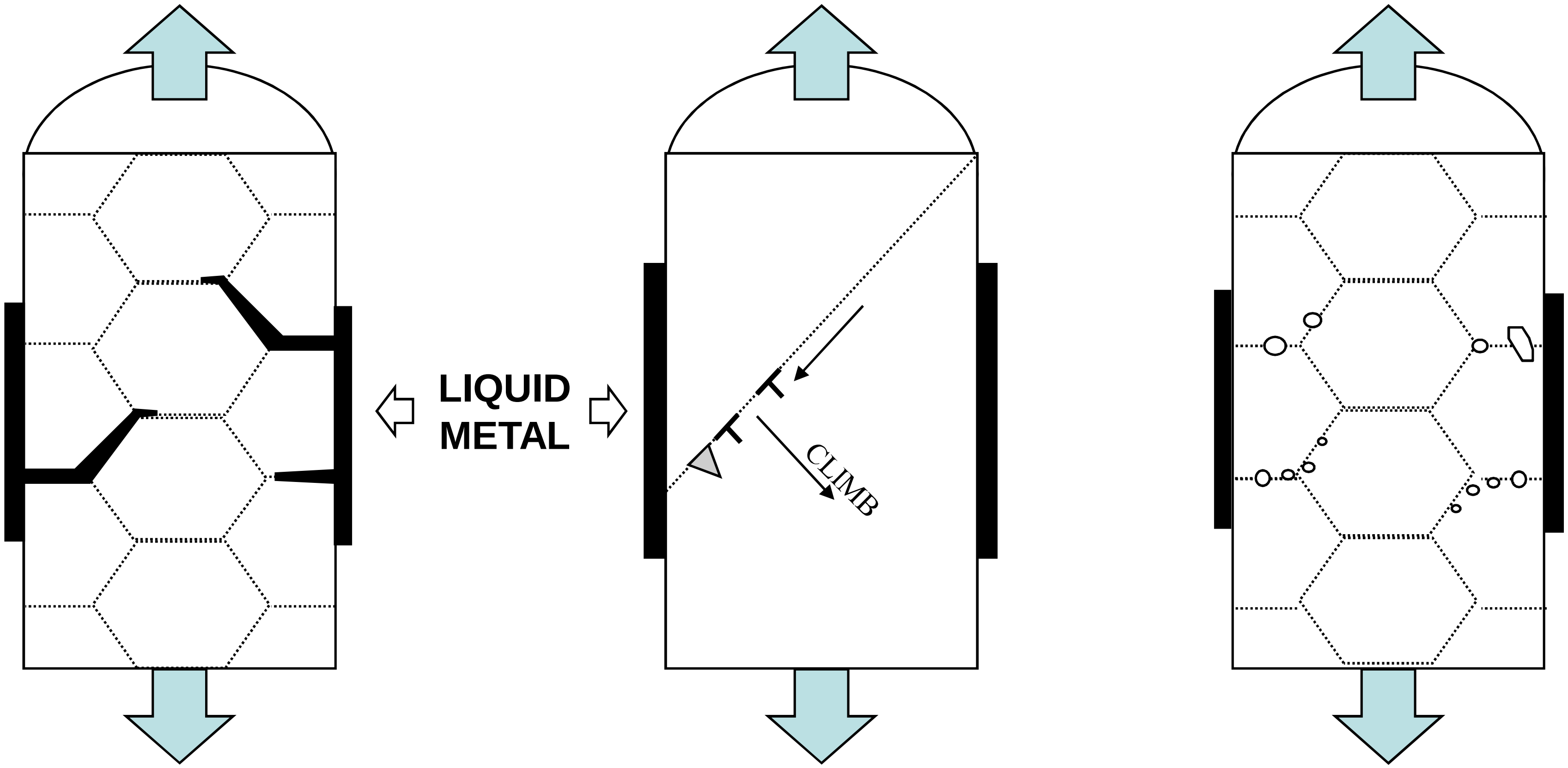
EVEN A SINGLE DROP CAN CAUSE RATHER FAST FAILURE



"EMBRITTLEMENT" ? PREMATURE FAILURE !



Three Forms of LME : Cracks Growth, Creep and Voiding



CRACKS

CREEP

VOIDS

LIQUID METAL

STRESS

“A hypothesis is a novel suggestion that no one wants to believe. It is guilty , until found effective”.

Edward Teller

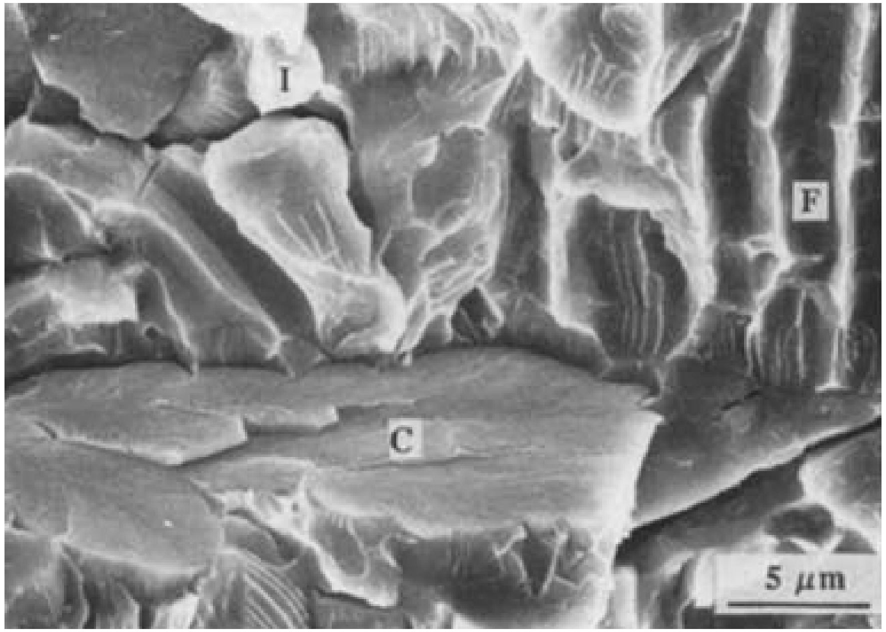
Outline

1. Introduction : LM Induced Failures
2. LME: non-electrochemical mode of SCC
3. LME: the problem of subcritical crack kinetics
4. TEM / SEM. Fractography. Acoustic Emission
5. Surface Energy and GB segregation effects
6. Dissolution-condensation mechanism of LME
7. Summary

LME was reported for

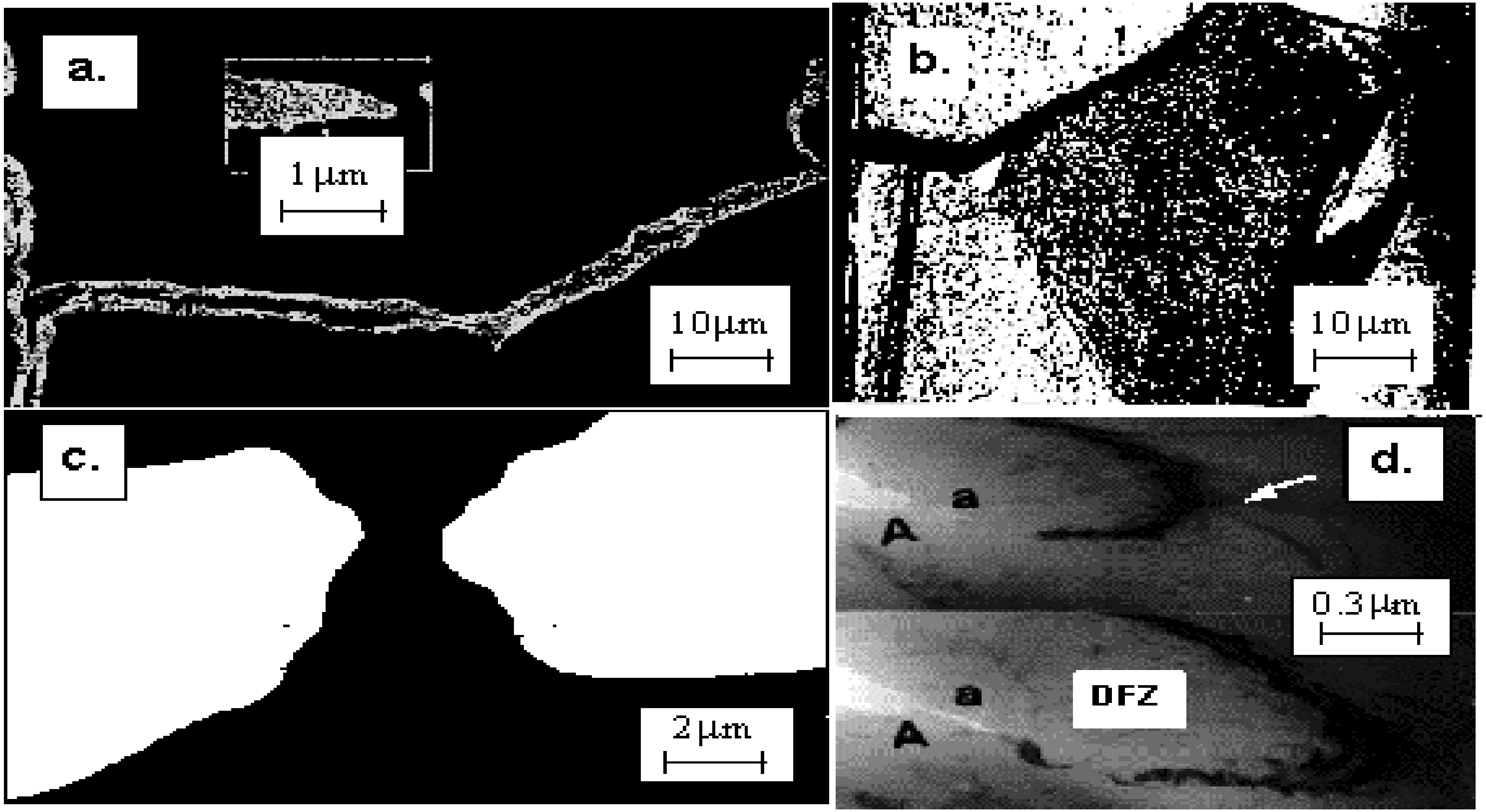
- *Single-crystalline* , poly-crystalline and *amorphous* metals
- All types of phase diagrams “SM –LM”, in particular, of simple eutectic type *without chemical compounds*
- Variety of fracture surfaces : from featureless trans- and inter- crystalline cleavages to *dimpled o*r heavily *faceted*

Trans-crystalline (C) and Inter-crystalline (I) areas in the fracture surface of Ti-6%Al -4%V broken in liquid Hg (S.Lynch)



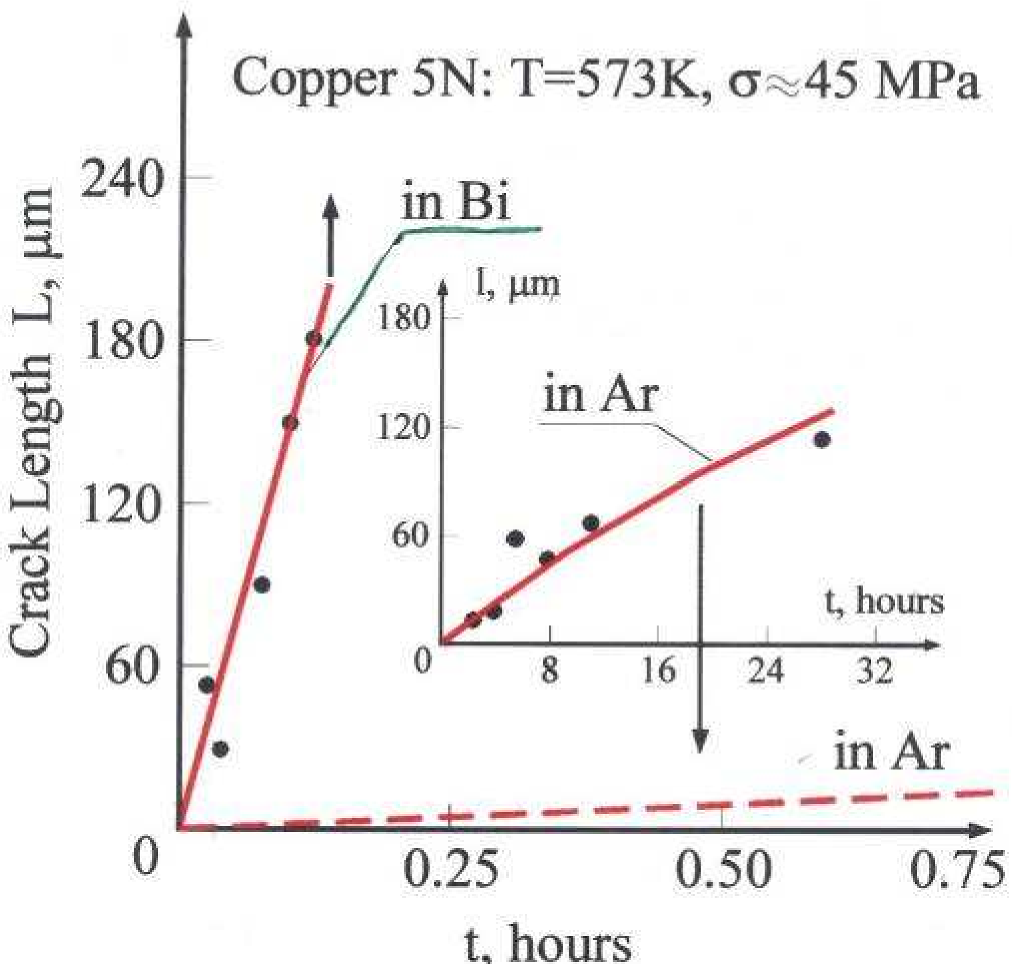
TEM replica

SEM / TEM Observations of Blunted Cracks

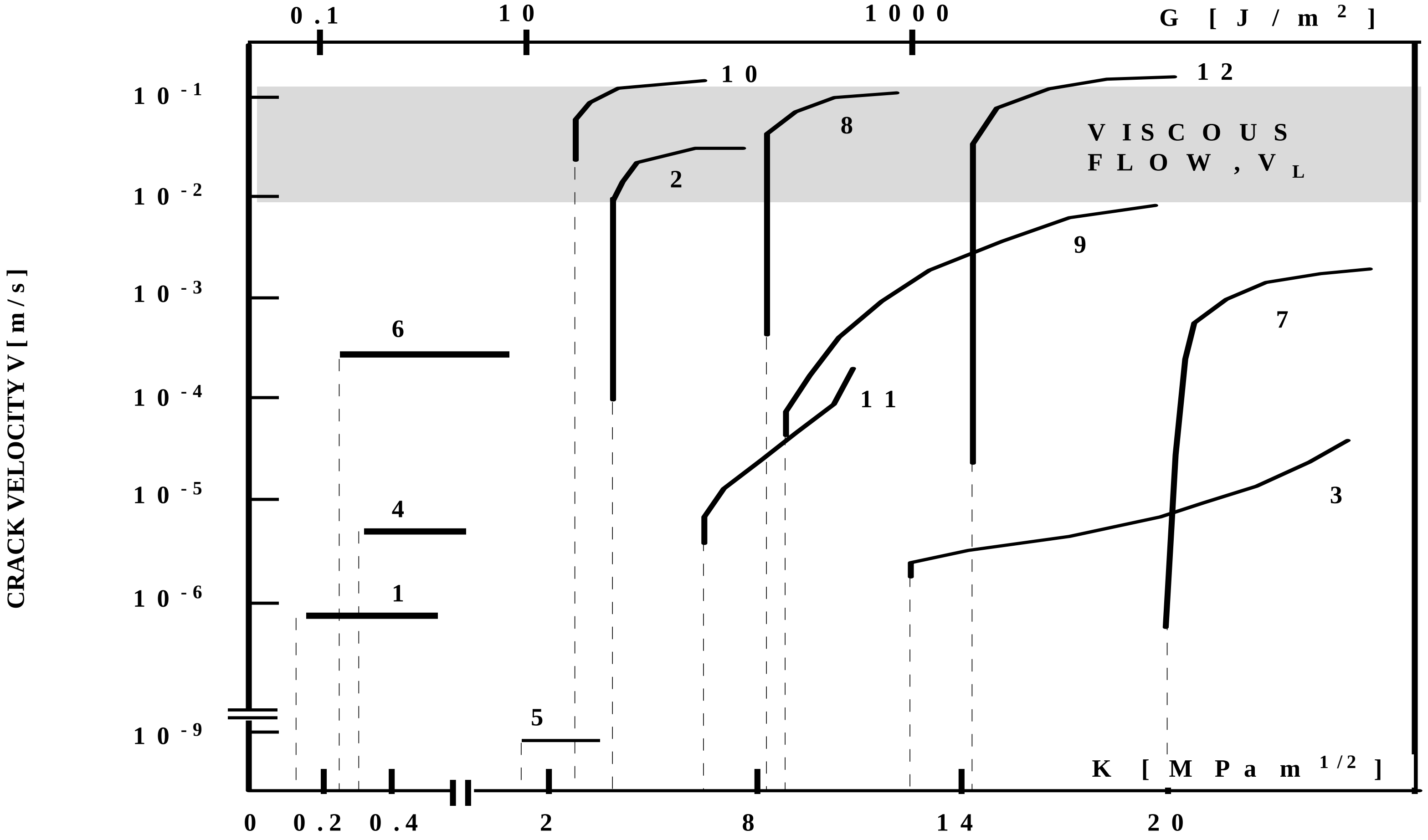


- a, c: Cu in Bi, 280-300C (a; Glickman ***et al.,*** ***c;*** ***Vook***)
- b: Cu in Ar, 300C (***Cherepanov et al***.)
- d: single crystal Al in Ga, 50C (***Su Y.J. et al***)

Liquid Bi Accelerates Subcritical Crack Growth in Cu by 300 times



Crack Velocity V [m/s] vs. stress intensity K under LME



***Solid metals**: 1 - Cu 99.999; 2-5-α-brass; 6 - Zn, single crystal; 7 - Ti alloy 8Al-1Mo-1V; 8 - Al alloy 1100-0; 9 - Al alloy 6061-T651; 10 - Al alloy 7075-T651; 11 - Al, bicrystal; 12 - Ti alloy 8Al-1Mo-1V,*

cf. with 7 for the same Ti alloy tested in 10M HCl water solution

Liquid metals: 1: Bi, 2-11:Hg . Curve 1 relate to T = 573K, all other -to room temperature

Activation Energy [eV] of subcritical crack growth (tip reaction control)

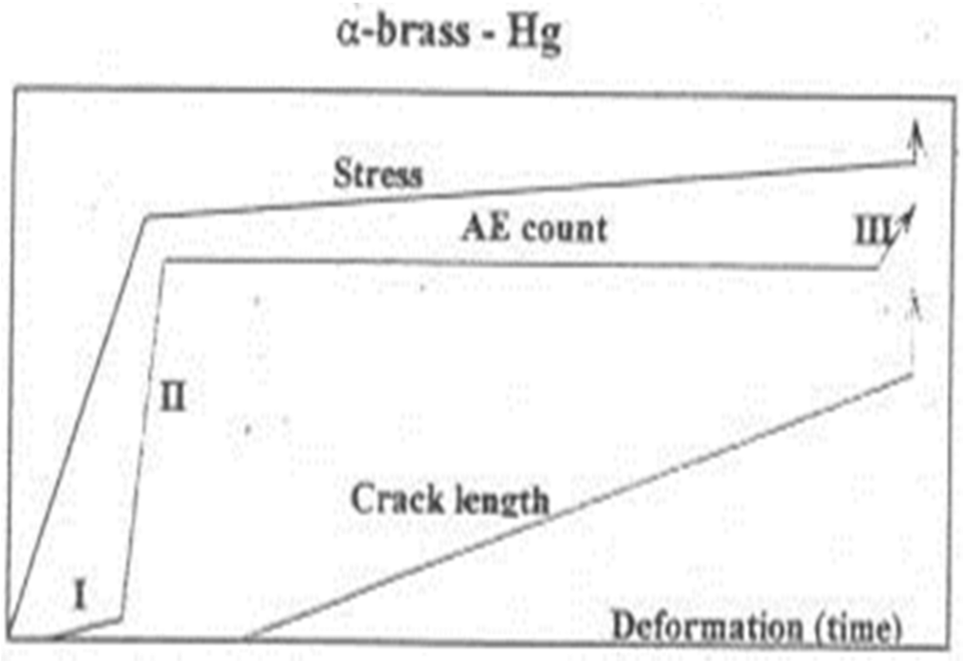
Cu in liquid $(Bi_{0.5}Pb_{0.5})$	**0.4 ± 0.05**	*E. Glickman et al., 2000*
Al 5083 in Hg	**0. 25**	*R. Clegg, 2007*
α-brass in Hg	**0.14**	*M. Kamdar, 1983*
Al-6061-T651 in Hg	**- (0.1 ± 0.02)**	*M. Kamdar*, 1983

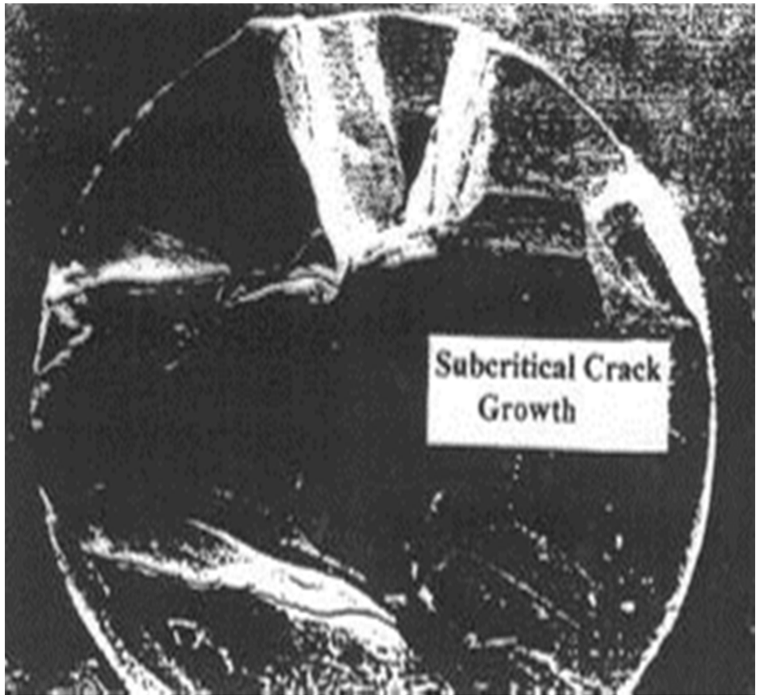
Activation energy seems to be too small for any relevant solid state process…

…but is compatible with the '*dissolution – diffusion – condensation*' scenario

LME of α-Brass in Hg : Burst Acoustic Emission does not accompany subcritical crack growth under constant load rate

(V. Igoshev , A. Braginsky, E. Glickman)

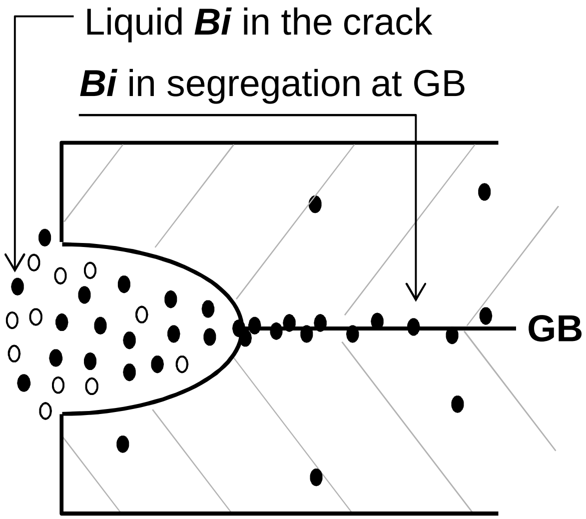


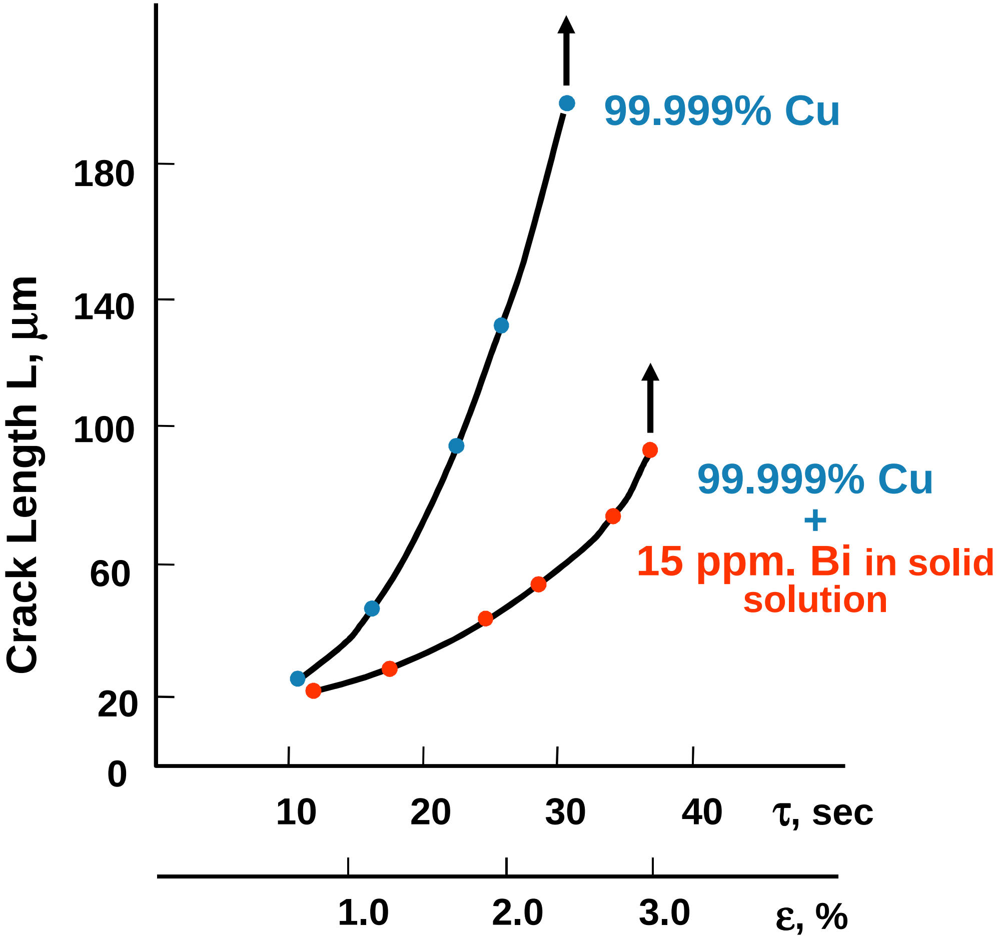


“Bismuth Against Bismuth”

or SELF-protection effect (reported also for Al-Ga system)

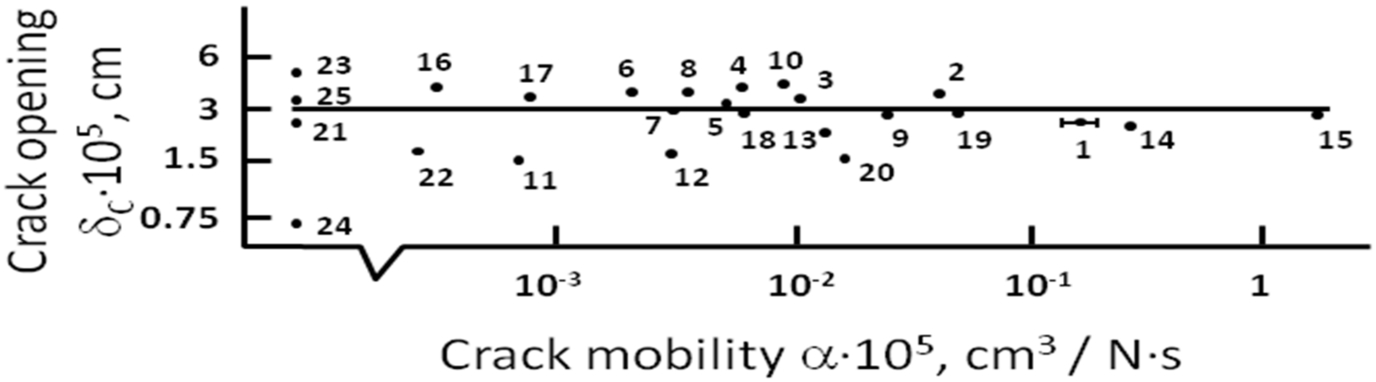
Glickman et al.





Bi segregation at GBs of Cu is known to reduce GB cohesion… however Bi segregated at GBs mitigates LME caused by liquid Bi

LME of Cu in Bi_xPb_{1-x} Melts



Conclusion:

Acceleration of subcritical stage – rather than reduction of fracture toughness – is the major factor in macroscopic manifestations of LME

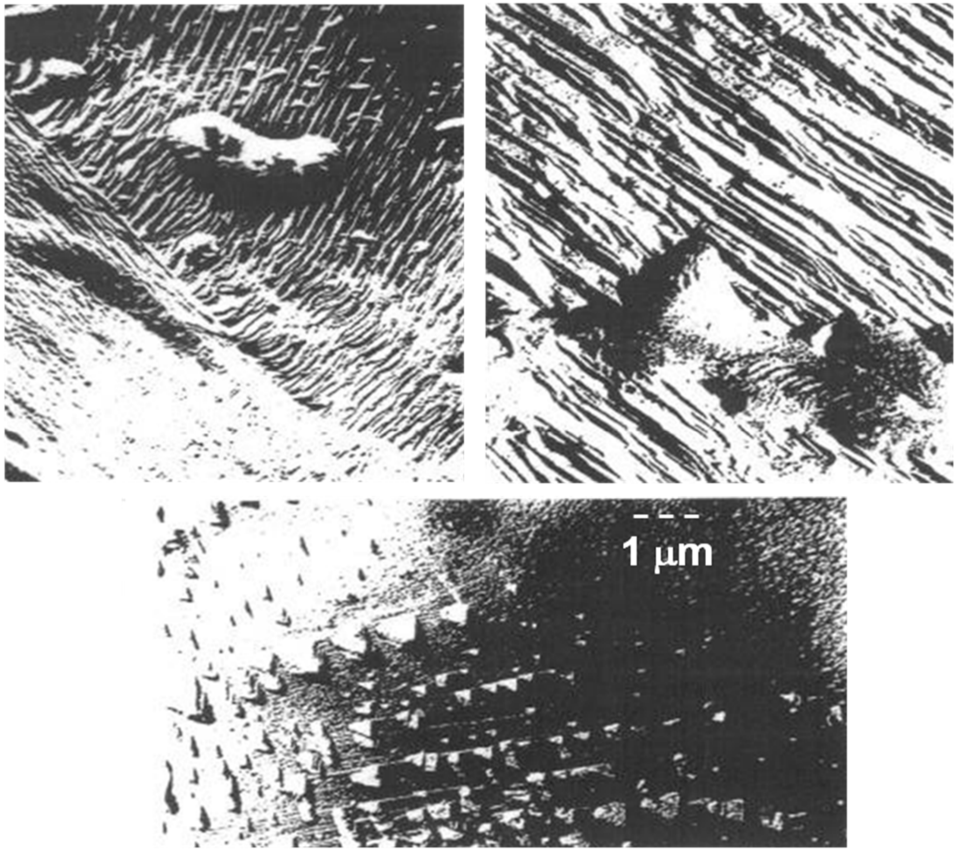
Failure in Liquid Metals is Faster because Subcritical Cracks are Faster

- The drop in the time-to-failure $\mathbf{t}_{\mathbf{f}}$, strain- to-failure $\boldsymbol{\varepsilon}_{\mathbf{f}}$, and failure stress $\boldsymbol{\sigma}_{\mathbf{f}}$ all resulted from acceleration of subcritical cracks which have LMs in their cavities .

- The fracture toughness G_{IC} is not sensitive to presence of liquid metals

Which Are the Accelerating factors and Kinetic mechanism?

Fractograms of GB fracture of Cu+0.05% Sb in liquid Bi

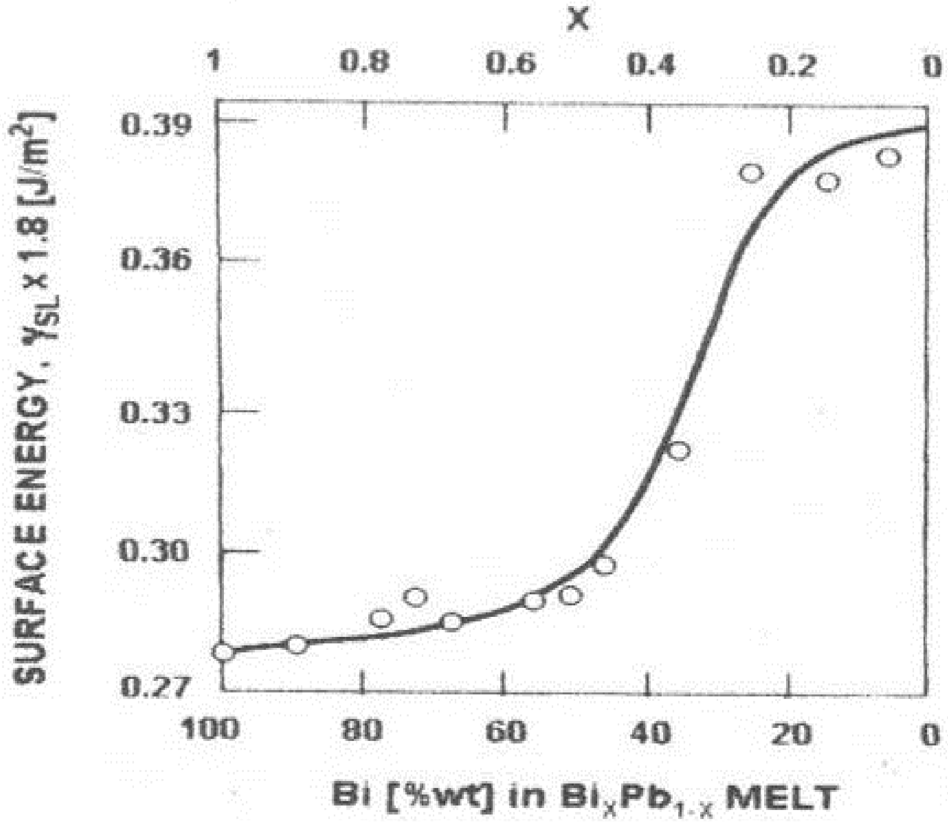


Intergranual Failure
of Cu + 0.05%Sb
in liquid Bi: σ = 47 MPa , T = 573K,

TEM on replica
A.Cherepanov ,L.Tuzov,
E. Glickman

Faceting and dislocation etch pits suggest
Fast Mass Transfer through Liquid in the Crack cavity

A new turn : experiments with "solid Cu -liquids Bi_xPb_{1-x}" system showed that the *surface energy* γ_{SL} at the solid /liquid interface is *critically important*



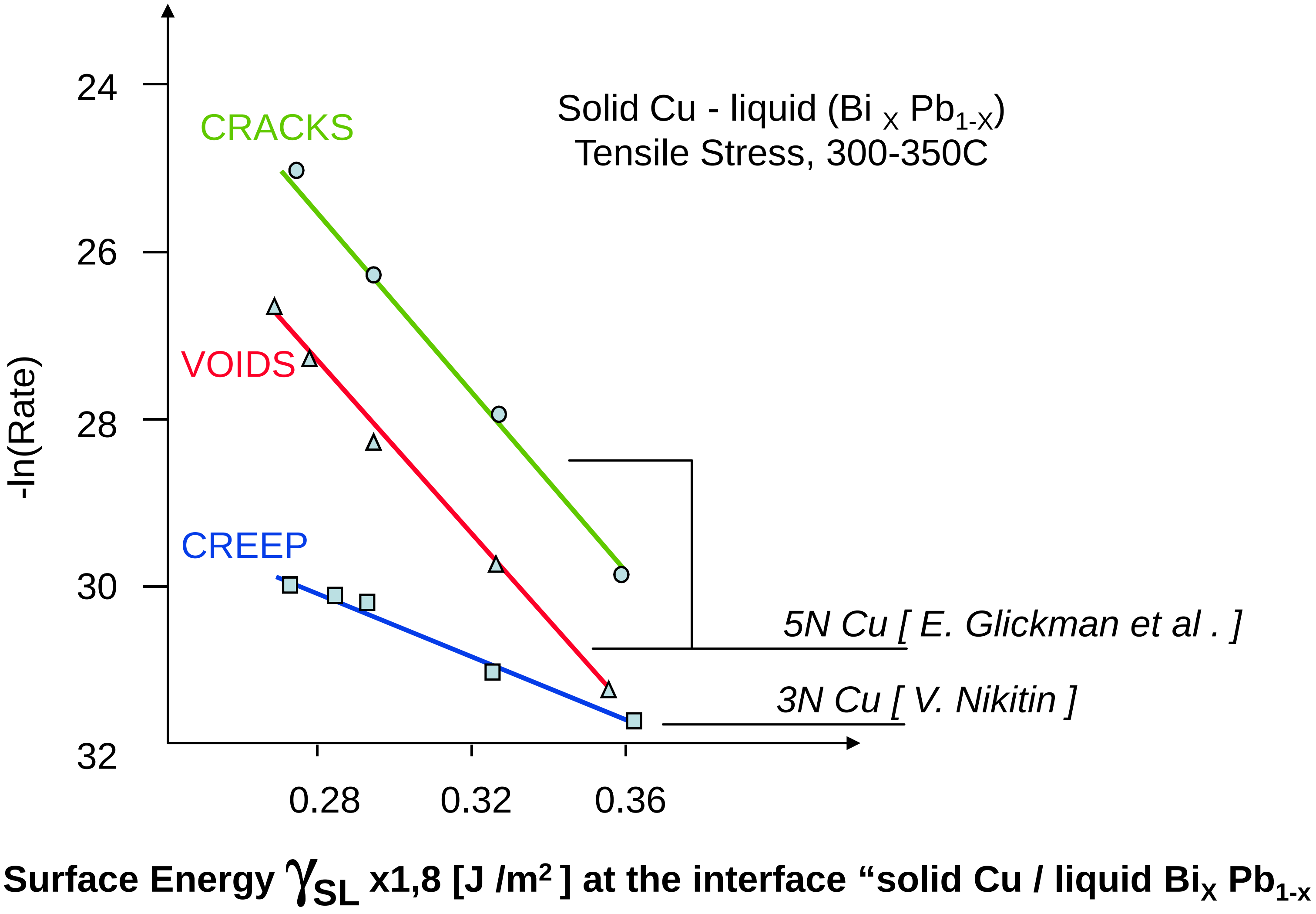
Specific Surface Energy γ_{SL} [J /m^2] at 350°C

Solid Cu-Vacuum:	**1.6**
Solid Cu-Liquid Bi:	0.16
Solid Cu-Liquid Pb:	0.21

*Liquid Bi and (to less extent) Pb are *strong surfactants* to Cu.

**Surface energy γ_{SL} can be changed by varying Bi/Pb ratio in Bi_XPb_{1-x}

Surface Energy Effects in LME: the rates of crack, voiding and creep ALL increase exponentially with reduction in γ_{SL}



Rhebinder Effect?

Dissolution /Condensation mechanism of LME: Robertson –Glickman Model (RGM)

- **W.M. Robertson (1966)** :

\- *elastic* **cracks grow by Dissolution - Diffusion – Condensation mechanism (DCM)**

\- **LMs in the crack cavity act as fast diffusion pathway**

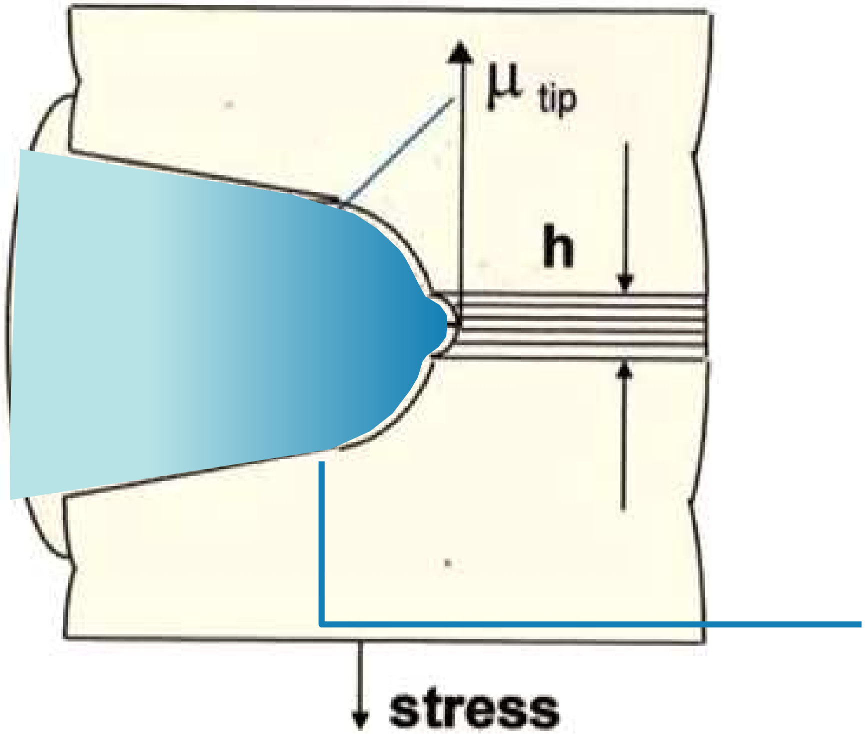
- **E. Glickman (1976,2003, 2011…):**

\- **cracks grow by DCM**

\- ***plasticity at the crack tip*** **affects** μ_{tip} **and grad**$\mu \sim \mu_{tip}$ **/COD**

\- **wetting by liquid metals causes** ***atomic roughening*** **of solid - liquid interface and favors thus DCM**

The Gist of Dissolution-Condensation Mechanism (DCM)



Concentration Gradient of SM in LM

∗Stress-related chemical potential μ_{tip} at the tip drives local dissolution , out-of-the-tip diffusion and re-condensation of SM atoms at the crack banks.

∗Liquid metal in the crack acts as fast diffusion pathway and causes hence fast crack growth.

∗Small opening of the channel **h** at the crack front favors large μ_{tip}

.

Two Reasons for the Accelerating Action of Liquid Metals

1.Diffusion in Liquid Metals is Very Fast

▼

…causes fast stress- induced mass transfer out of the crack tip

2.Wetting Induced Surface Roughening

▼

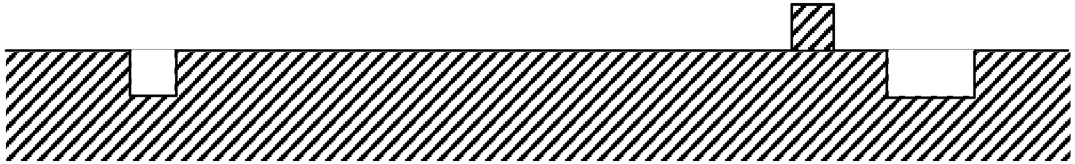
…causes fast detachment /attachment at the solid-liquid interface

▼

- Fast Dissolution/Condensation in Crack Growth
- Fast Consumption/Production of Vacancies in Creep and Voiding

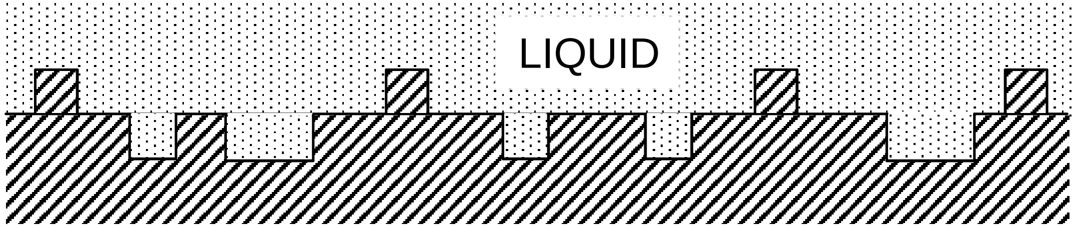
Wetting Induced Surface Roughening
Depends on the Surface Energy, γ

$C_j = \exp(-A\gamma / kT)$: equilibrium concentration of kinks and adatoms



Solid-Vapor Interface
$\gamma \approx 1 J / m^2$; $\mathbf{C_j} \approx 10^{-5}$

SMOOTH



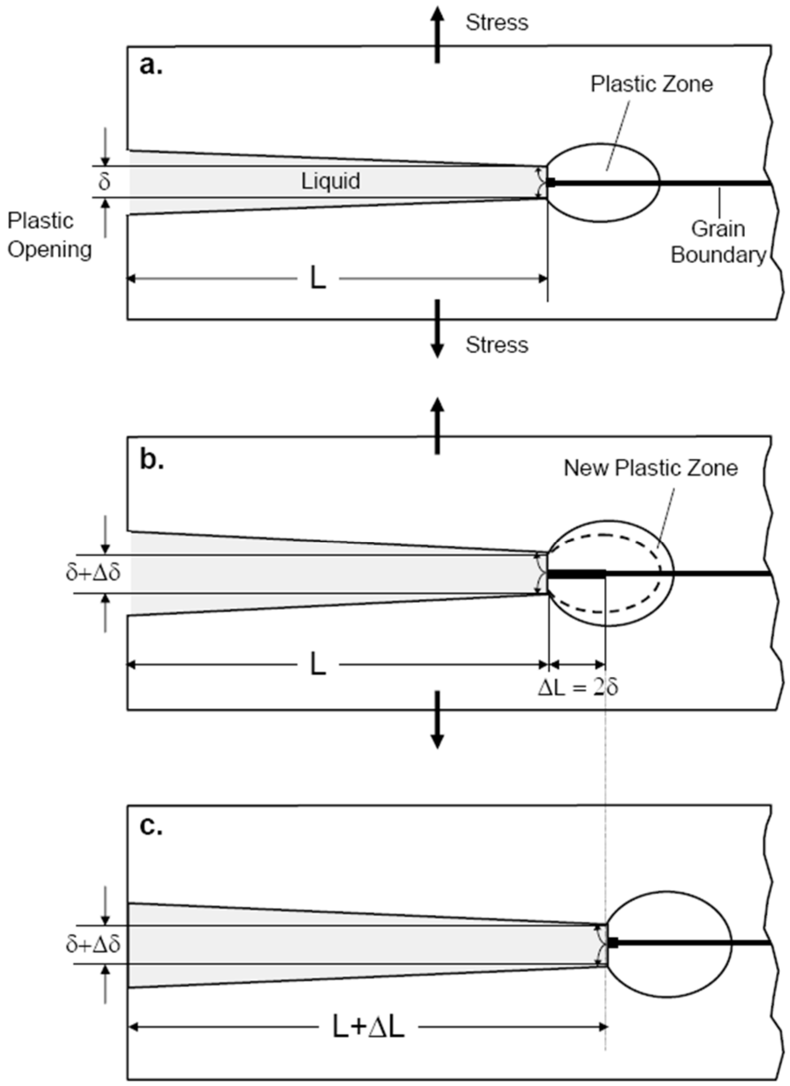
Solid-Liquid Interface
$\gamma_{SL} = 0.1 J / m^2$; $\mathbf{C_j} \approx 10^{-1}$

ROUGH

Detachment / Attachment
Interface Reactions
Accelerate with $\mathbf{C_j}$

Dissolution and Vacancy Formation at Surface

DCM: Robertson-Glickman model, 2013



Essential Physics

Crack velocity: $V = -M \cdot \mathrm{grad}\ \mu$

Mobility: $M = D_L C_{\infty L} C_J / kT$

Driving force: $grad\ \mu \approx \mu_t / \delta$

Diffusion Length: ~ ($\delta = COD$)

Taken from fracture mechanics

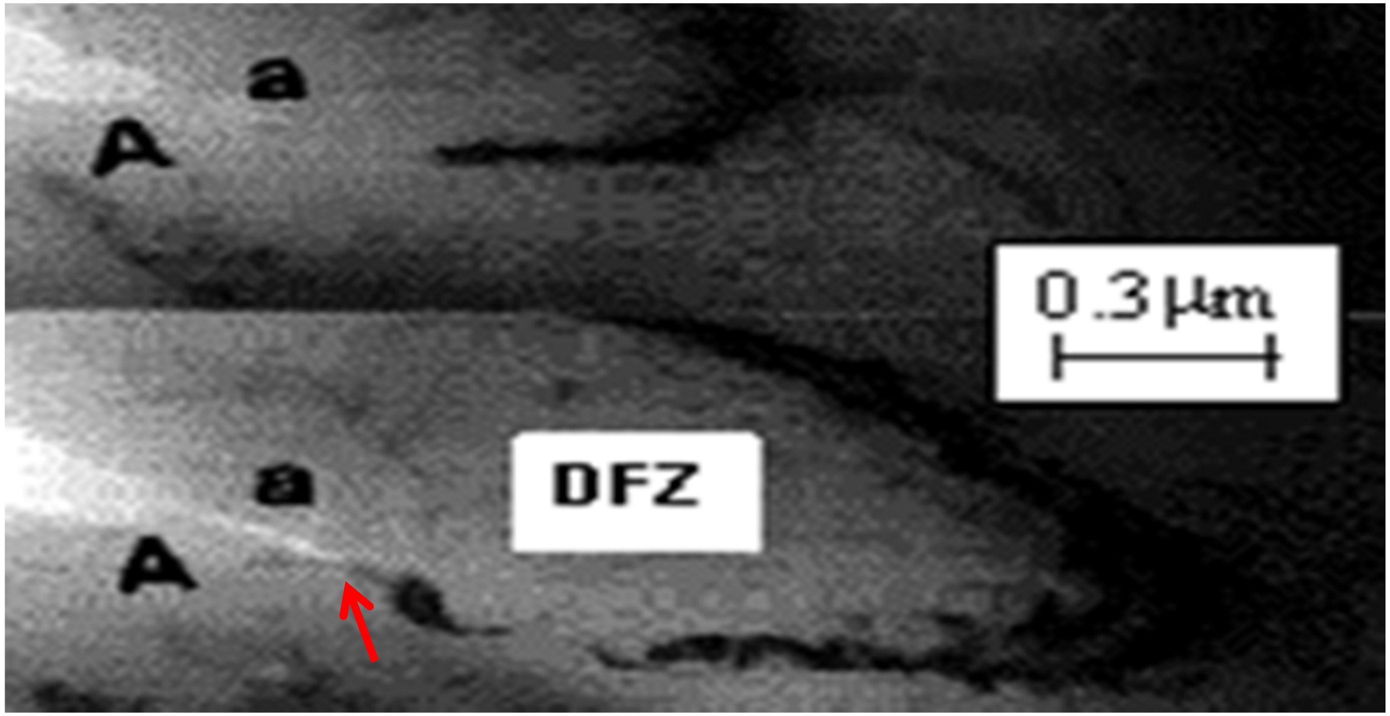
Chemical potential $\mu_t \sim K^2 / h$

$$COD = \delta \sim K^2 / \sigma_Y$$

As μ_t ~1/ h, cracks are not stable to emission of a narrow channel *h* ahead of the tip and can grow thus by “emission –plastic blunting-emission” process

See two next slides !

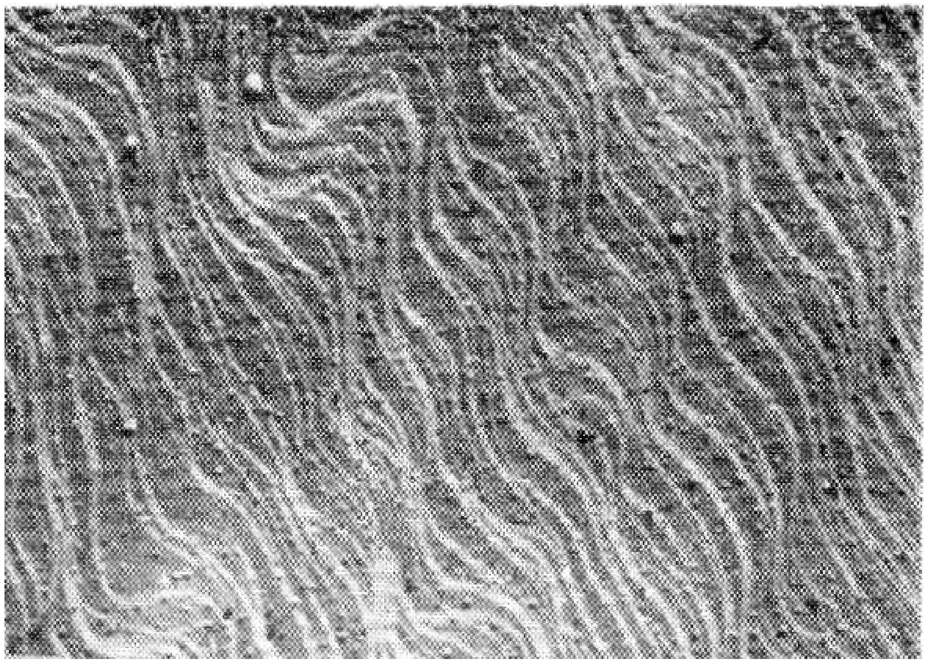
A Narrow Channel (h~10^{-6} cm) Ahead of the Blunted Tip



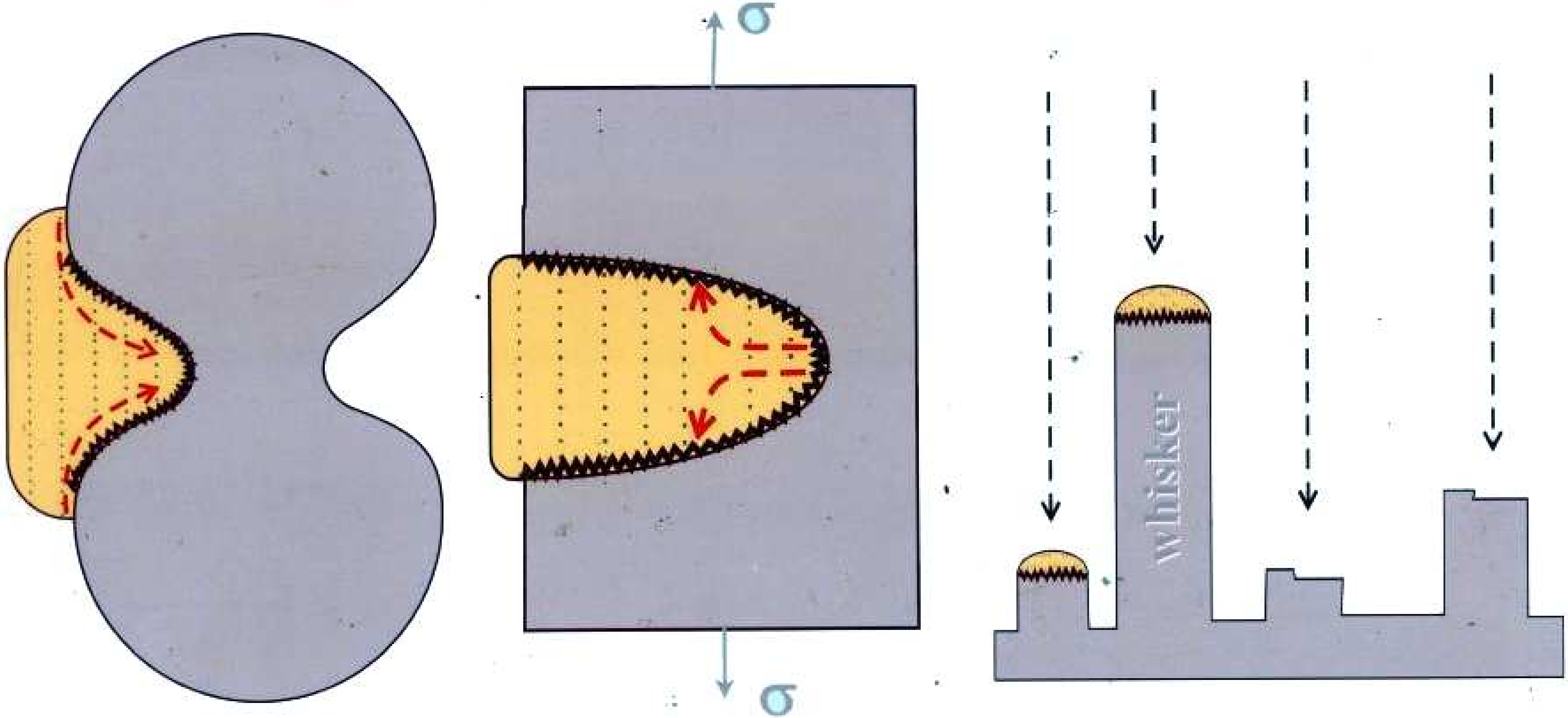
In- situ **TEM of a LME crack in Al single crystal under creep in (Hg + 3%Ga) at 323K for 5h (upper part) and 50h. *Su Y. et al*.**

Intergranular fracture surface of Cu after creep in liquid Bi at T=573K. X15000. TEM replica (A. Cherepanov and E. Glickman)

Slip markings suggest periodic crack blunting after $\Delta L \sim (0.1\ldots0.5)\ \mu m$



Liquid metal assisted



sintering

crack growth

VLS growth of whiskers

Accelerating factors:

1. Fast diffusion in liquid *2. Wetting induced roughening*

Crack Velocity V by DCM

$$V \approx (D_L\, C_\infty\, C_j) \cdot (\sigma_p / G) \cdot [\exp(\mu_t / kT) - 1]$$

Mobility Group   Yield Stress   Energy Balance Group

$$\mu_t / kT = (\omega / \mathbf{h})\,(G - G_{TH}) / kT$$

Strain energy release rate, $G = K^2/2E$

$$Activation\ Energy \leq (H_{DL} + H_{C\infty} + H_{Cj}) < 0.5eV$$

Crack Kinetics by DCM

The crack kinetics predicted by DCM describes all types of V(K) diagrams and captures the velocity V (K) for soft , single-phase metals

Fast Cracks in High Strength Alloys : difficult to explain within pure DCM

1. Fast cracks V >10^{-2} ...10^{-1}... cm/s in high strength alloys
2. Large threshold G_{TH} >> 0.5 J/m^2 in high strength alloys

Fast Cracks

Crack velocity in high strength alloys **is** $V \approx 10^{-1}$ m/s

Pure DCM **predicts** much smaller $V_{DCM} < (10^{-1} - 10^{-2})$ cm / s

Why?

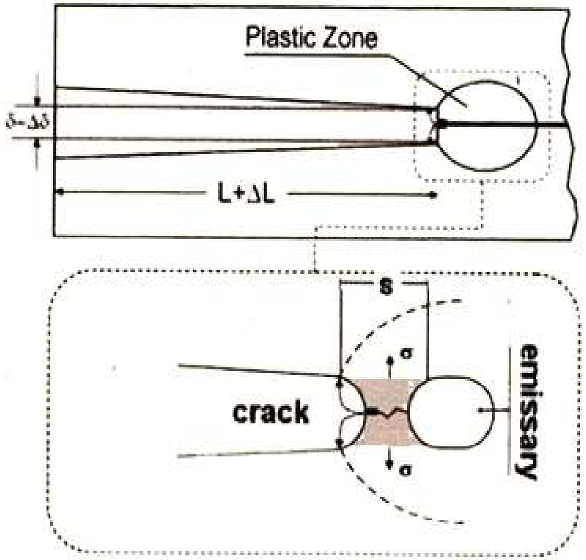
Answer

Combination of DCM with shear instability

(as proposed by J. Krafft for SCC)

$$V = k \cdot V_{\mathrm{DCM}} \qquad k = 8 / \varepsilon [(\theta / \sigma)-1] \sim (10^2 \div 10^3)$$

for high strength alloys with low strain hardening $\theta = d\sigma / d\varepsilon$



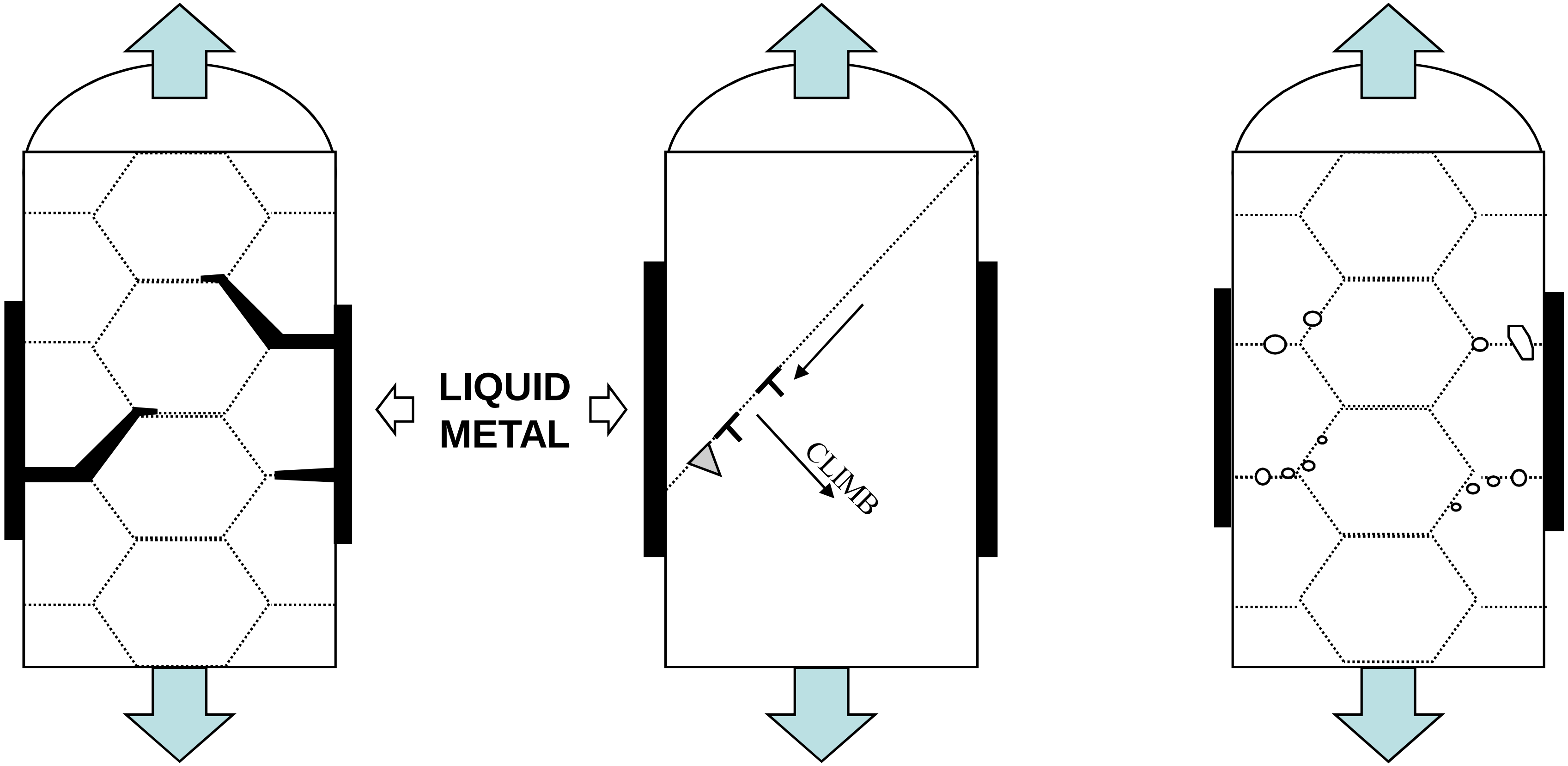
Stress induced dissolution causes thinning and rupture of the 'internal neck' in the plastic zone.

Three Forms of LME : Cracks Growth, Creep and Voiding

CRACKS

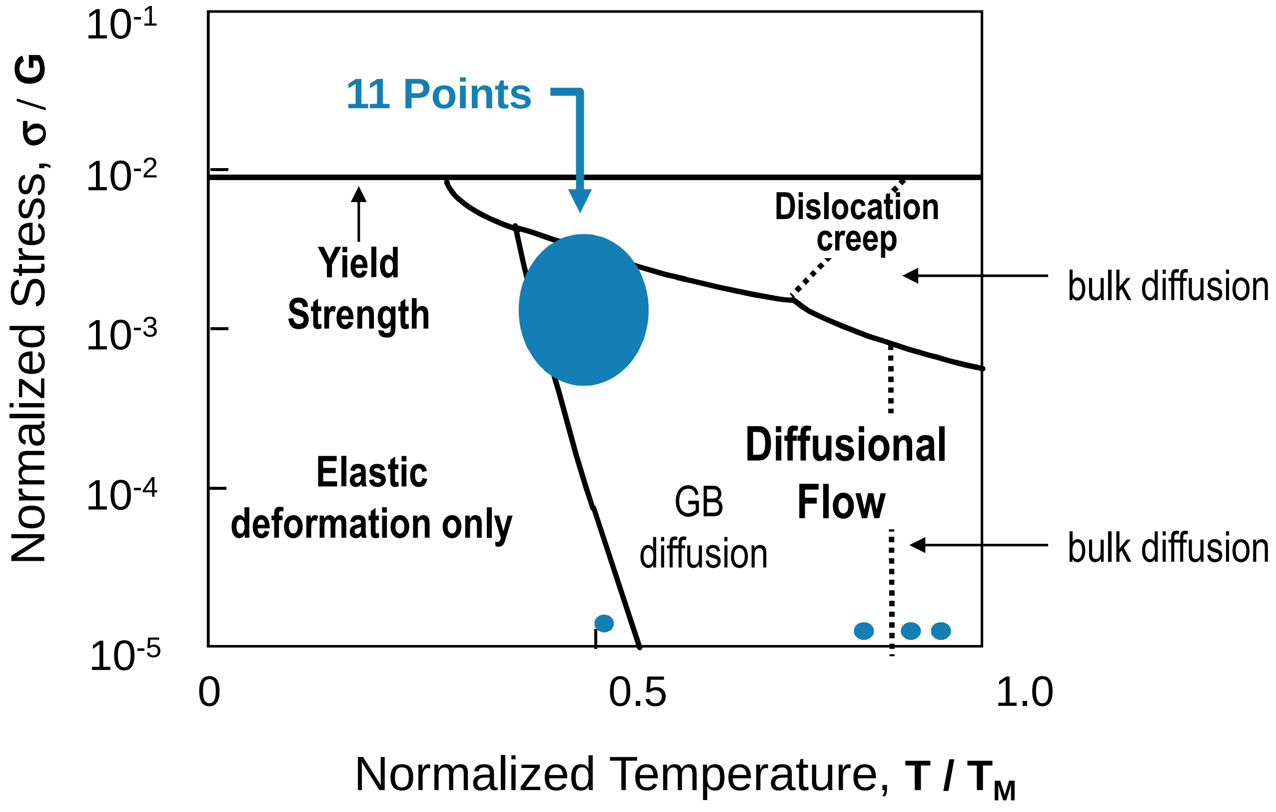
CREEP

VOIDS



STRESS

LM Accelerated Creep On The Creep Mechanism Map



Wetting Induced Surface Roughening
Depends on the Surface Energy, γ

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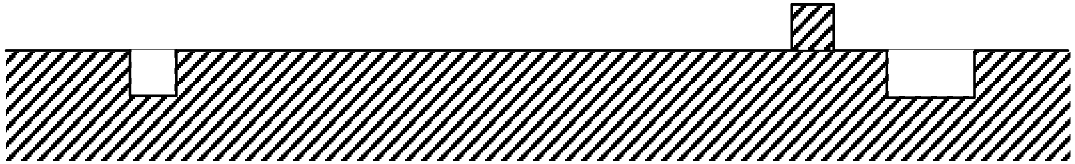

Solid-Vapor Interface
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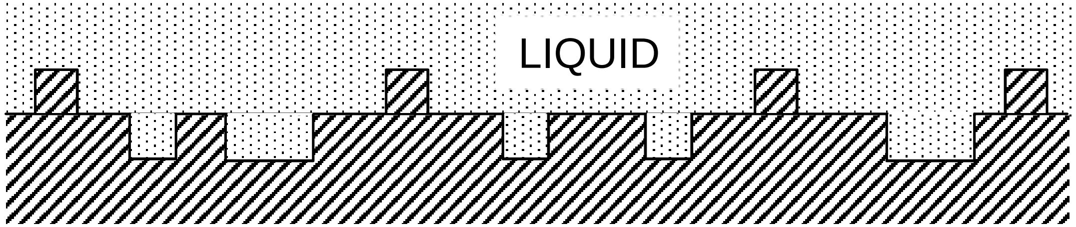
SMOOTH



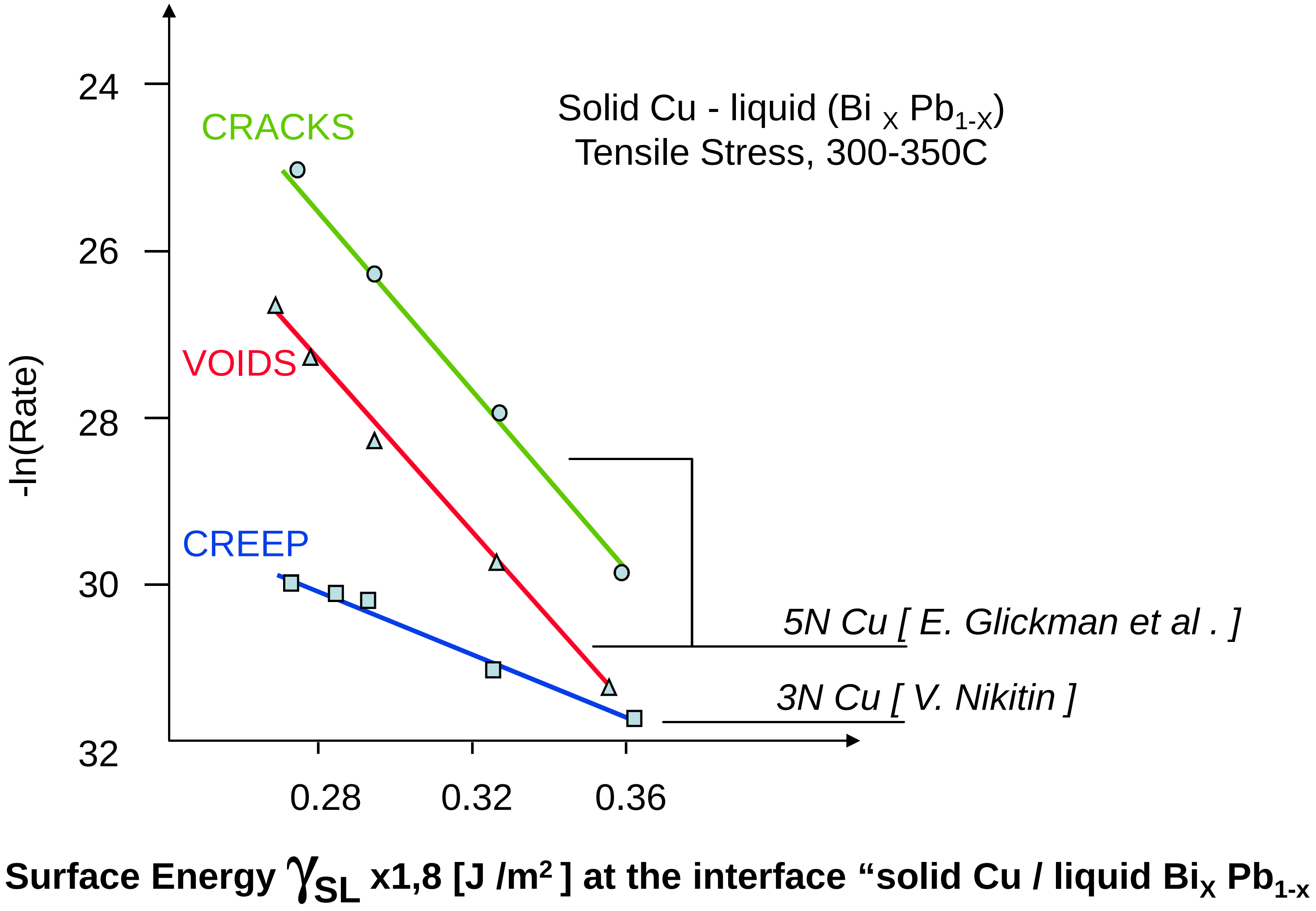
Solid-Liquid Interface
$\gamma_{SL} = 0.1 J / m^2$; $\mathbf{C_j} \approx 10^{-1}$

ROUGH

Dissolution and Vacancy Formation at Surface

Detachment / Attachment Interface Reactions Accelerate with $\mathbf{C_j}$

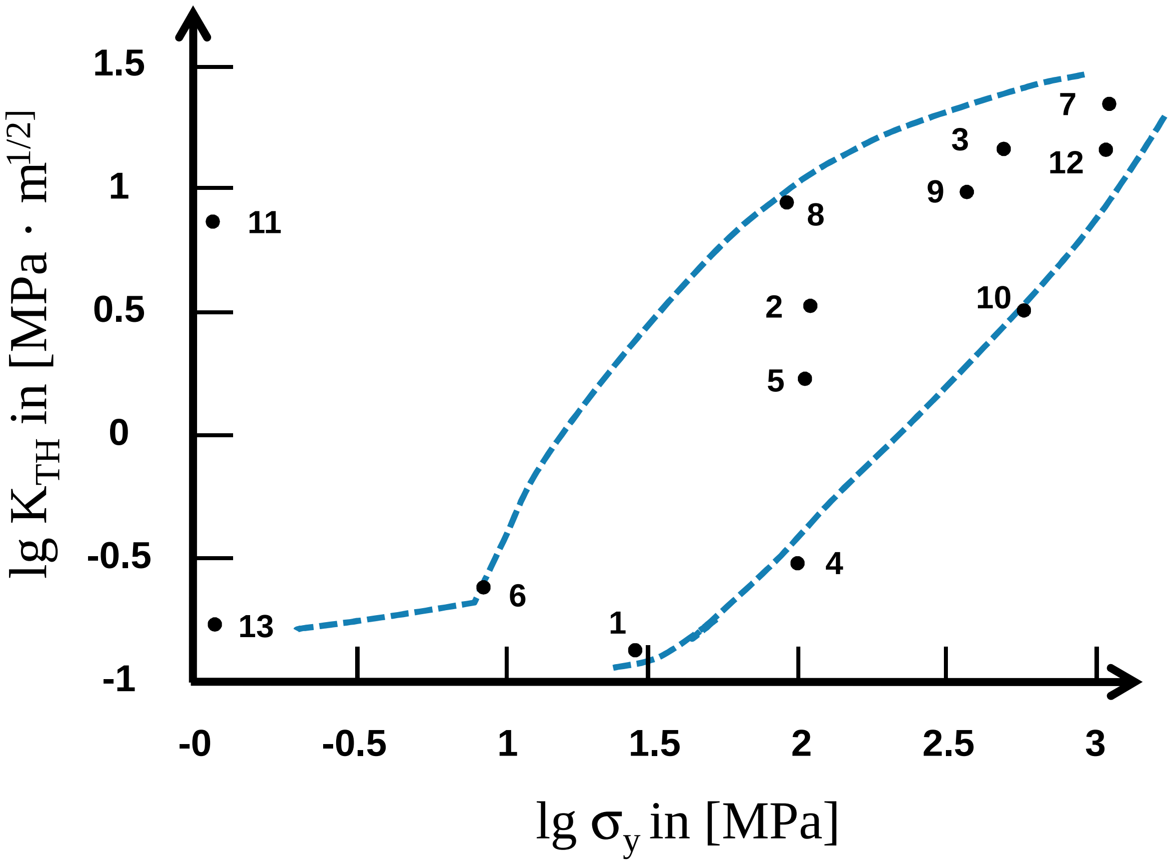
Surface Energy Effects in LME: the rates of crack, voiding and creep ALL increase exponentially with reduction in γ_{SL}



the Rhebinder Effect?

LME thresholds K_{TH} for Cu, Ti and Al Alloys tend to increase with the yield stress σ_Y .

Roughly, $(K_{TH}/\sigma_Y)^2 \approx 30\mu m = R^*_{pl}$: critical size of plastic zone



1-12 are from our V(K) compilation ; ;#13: Al bicrystal in Ga (W.Ludwig et al.).

#7 (SCC of Ti alloy in salt water) and #12 (the same alloy in Hg) show rather close K_{TH}’ .

Is K_{TH} under LME controlled *solely* by nucleation of emissary -microcrack ?

SUMMARY

1.LME is *non-electrochemical* mode of SCC. Studying LME gives the insights into the *unique role of stress as a driving force of* SCC

2. Close similarities between the proposed mechanism LME and the mechanisms of liquid phase aided sintering and crystal growth.

3.DCM captures the major features of LME in low-strength metals, including the important role of surfactant LMs . The only free parameter of the model is the width h of the channel ahead of the blunted crack. It should be ~10^{-6} nm, or less

4. Coupling DCM with shear instability in the plastic zone is requiredT in order to fit the LME data for fast cracks and large thresholds G_{TH} in high-strength alloys.

5. Available observations -scarce as they are - suggest that G_{TH} in Cu- , Al- and Ti –based alloys tends to increase with the yield stress.

TIME to LME failure under creep scales as $1/\sigma^2$

$$t_f = \left(1/\alpha\sigma^2\right) \times \boxed{\left(K_c{}^2/\sigma_y\right)}$$

Confirmed by V. Nikitin and by E. Glickman et al. , Soviet Phys. Journ., v.23 ,1980,364

LME and Radiation Damages:

- Radiation Embrittlement: K_{IC} ↓
- Radiation Hardening: σ_y ↑

A candid professor confesses
That the secret of half his success is
Not the science, as such,
Nor its marvels so much ,
But his wild , irresponsible guesses.

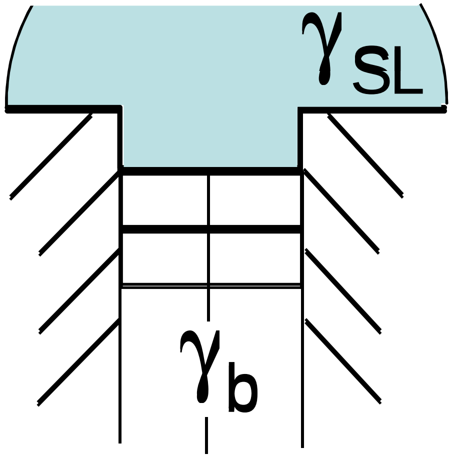
EFFECT OF EQUILIBRIUM GB SEGREGATION

OBSERVATIONS

Sb, B, Ce and even Bi (!) in Cu, all slow down GB cracks in liquid Bi

EXPLANATION

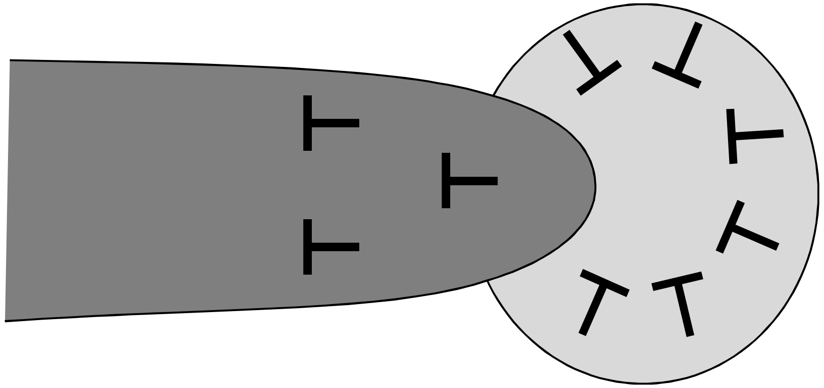
1. Kink Formation Energy is lower at GB: $U = A_{SL}\gamma_{SL} - A_b\gamma_b$
2. Equilibrium GB Segregation **always** reduces GB Energy, γ_b
3. Dissolution Rate $\propto C_j \propto \exp \gamma_b$



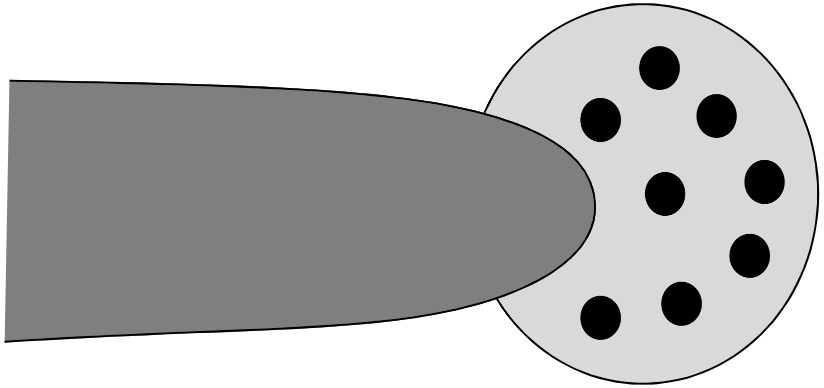
A_b : the decrease in the GB surface area

Crack Shielding / Bridging Can Explain Large G_{TH}

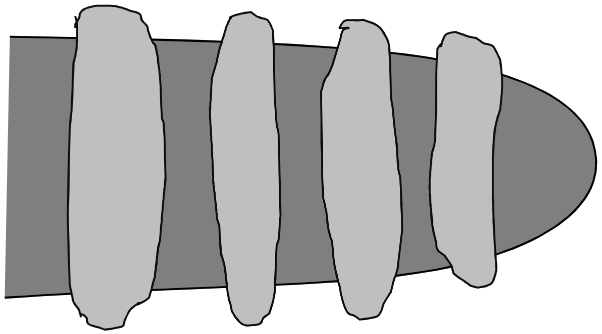
a. **Dislocation Cloud**



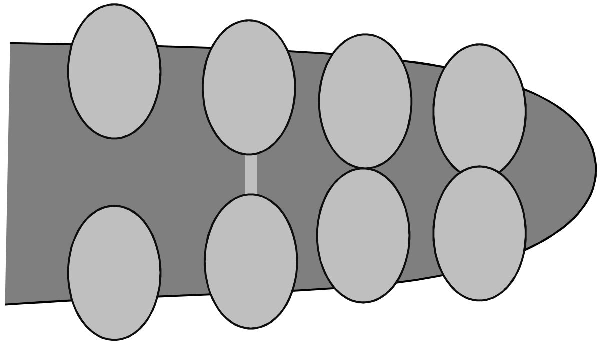
b. **Ductile Phase**



c. **Precipitate Bridging**

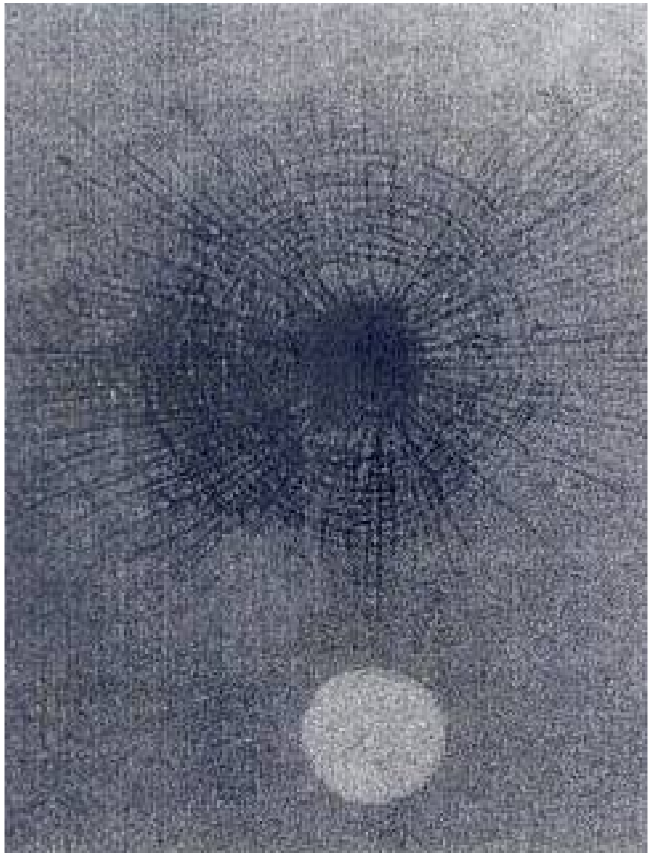


d. **Precipitate Bridging**



Liquid Hg Reveals Residual Stress

around the cup made by plunger in Al- 2024-T4



White: without Hg

W. Rostoker, J. McCaughey, H. Markus
Embrittlement by Liquid Metals, 1960, NY

DCM under residual stress explains nano-metric GB films

“Individual grains of Al come apart as the molten Ga whizzes down the boundary”

M. Ashby, D. Jones, *Engineering Materials 2, 1988*

“Invasion-like process… the volume occupied by the liquid metal leads to deformation and relative separation of the grains”

W. Ludwig et al. *Phys. Rev Lett. 95 (2005)*

OBSERVATIONS *(W. Ludwig et al)*

- Ga penetration in Al bicrystals. d_g (separation of adjacent grains) $\approx h_{GA}$ (thickness of Ga)

INTERPRETATION

“Invasion-like process” is unnecessary. The findings are consistent with DCM

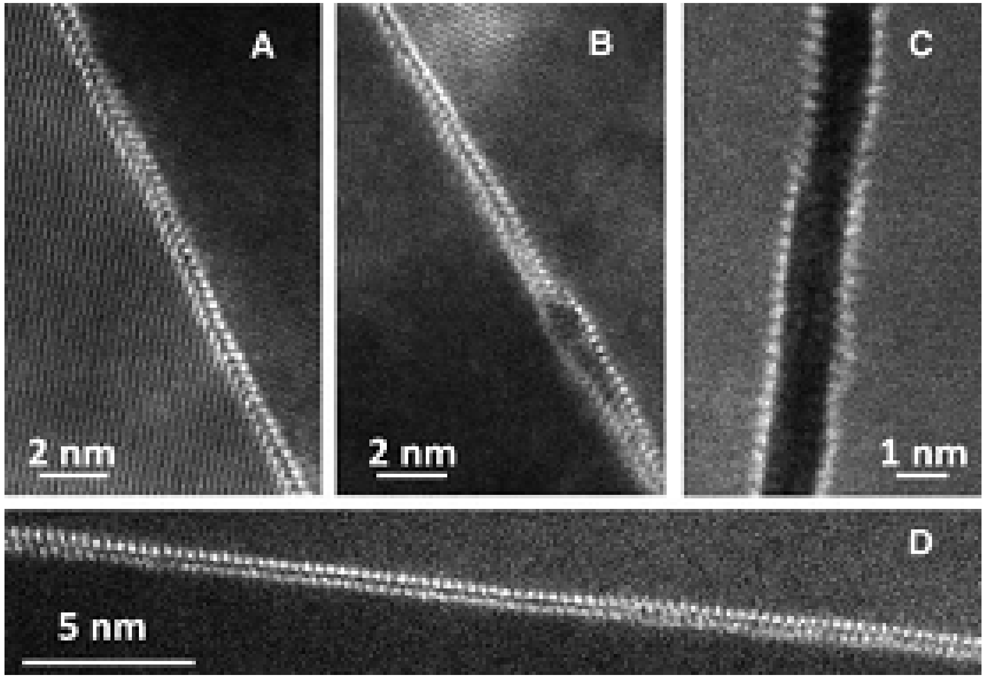
***E. Glickman**. Z. Metallkd., 96 , 10 (2005)1204.*

Within DCM liquid metal phase enters the cavity of the GB crack that was pre-opened by the plastic blunting and elastic deflection

$$h_{GA}(r/L) = d_g(r/L) = \delta_T(r/L)$$
$$\delta_T(L) = (K^2/E\sigma_{pf})\cdot[1+(\sigma_{pf}/\sigma)\cdot(\rho/L)^{1/2}]$$

The crack opening $\delta_T(r/L)$ predicted by DCM fits well with the experimental profiles of Ga layer

CONCLUSION: DCM rather than a mysterious “Invasion”



A, B and D : HR STEM micrographs showing *two mono-layers of Bi absorbed at random GBs of Ni poly-crystal annealed at 700°C in presence* of liquid Bi and quenched .
C: Presumably, decohesion of the GB occurred during TEM specimen preparation. *Jian Luo, et al, SCIENCE, v. 333, 23 ,2011, 1730*

Chemical Potential μ_{tip}

$$\boldsymbol{\mu}_{tip} = -(\partial F/\partial n)_{N,T,\sigma} = (K^2/2E)\cdot(\Omega/h) = \mathbf{G\cdot(\Omega/h) \sim 1/h} \qquad (1)$$

K: stress intensity; G: strain energy release rate; Ω: atomic volume; ***h: the crack width at the front***

μ_{tip} enables linking Fracture Mechanics to diffusion Crack Kinetics

▼

μ_{tip} (K) ▸ grad μ_{tip} (μ_{tip}, tip geometry) ▸
▸ out-of-the-tip diffusion flux J (D_L,grad μ_{tip}) ▸ crack velocity V~J

Estimates

G ≈10J/m^2, h=10^{-6} cm . T = 300K; **μ_{tip} = 0.6 eV. exp (μ_{tip}/kT) >2.6 10^{10}**

With this, $C_{tip} \rightarrow 1$(saturation) *, **even for very low solubility limit C_{∞} given by specific phase diagrams, e.g. for $C_{\infty} \approx 10^{-7}$ (for Ti in Hg)***.

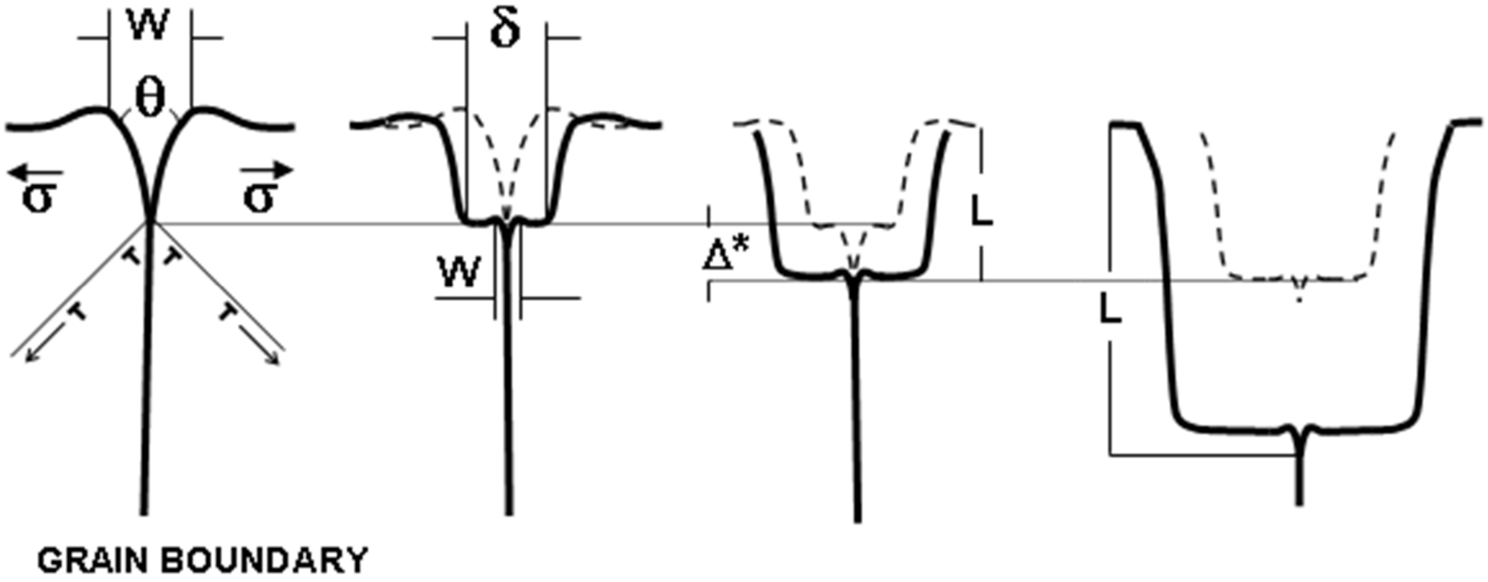
LME Mechanism: Concepts vs. Observations

Concept	Author(s)	At Variance With	Fails to Explain
Adsorption - Induced decohesion ▼ Ductile-Brittle transition	*Westwood et al*	Dimpled surface, effect of T, “Bi-against Bi”	LME specificity and the tip- reaction crack kinetics
Adsorption – Induced dislocation emission ▼ microvoid coalescence	*Lynch et al*	LME in amorphous metals, featurless / faceted fracture surface	LME specificity and the crack kinetics
GB Diffusion ▼ GB Wetting / Melting	*Rabkin, Vilenkin , Nam & Srolovitz*	LME in single crystals and amorphous metals. Fast cracks require unreasonable diffusivity D ~ 10^{-6} cm^2/s at RT	LME specificity and the crack kinetics

A unified LME mechanism should likely go beyond the scope of these concepts

Crack Initiation and Growth by 'GALOP' *

* **G**rooving **A**ccelerated by **Lo**cal **P**lasticity



- Plastic strain accelerates spontaneous Mullins grooving by changing boundary conditions for diffusion and deposition
- Small diffusion length in liquid Δ* << L → fast deepening. The smaller are the blunting distance Δ* and the dihedral angle θ, the faster the process.
- Small, if any, threshold K_{TH} for crack initiation
- N repetitions of "grooving + blunting"→ crack $L = N \cdot \Delta^*$

- **Threshold $G_{TH} = 2\gamma_{eff}$ for LME in several single-phase metals is comparable to intrinsic surface energy γ_{SL} of the solid/liquid metal interfaces in m.**

- **In aging alloys $G_{TH} \gg \gamma_{SL}$ and varies over 3 decades . We suppose shielding / precipitate bridging.**

Metal	*Environment*	*T, K*	*Experimental $\gamma_{eff} = mJ/m^2$*	*Refs.*	*Observation technique*
Zn single crystal	Hg	250-300	53±8	[1]	Controlled slow cleavage
Zn single crystal	Ga	300	42±13	[1]	Controlled slow cleavage
Al bicrystal 140°, <110> tilt GB	Ga	300	≤ 14	[31]	From the threshold K_{IC}
Ti alloy 8Al-1Mo-1V	Hg	300	$> 10^6$	[1]	From the threshold K_{IC}

SEE MORE DETAILS IN :

1.E. Glickman and M. Nathan, ***On the Kinetic Mechanism of Grain Boundary Wetting*** *,*
J. Appl. Phys., 85 , 1999 , pp. 3185-3191

2.E. Glickman ***, Mechanism of LME from Simple Experiments: From Atomistic to Life-Time***
In: NATO ASI Multiscale Phenomena in Plasticity, J. Lepinoux et al. (eds.) (2000) 383 Kluwer

3. E. Glickman , ***Mullins Grooving Accelerated by Local Plasticity as a Possible Kinetic Mechanism of Liquid Metal Embrittlement ,***
*Interface Science , v.**11** (2003) 451*

4. Glickman E., ***Fast Penetration of Ga in Al: Liquid Metal Embrittlement Near the Threshold of Grain Boundary Wetting****,*
Intern. Journ of Materials Research v. ***96*** *(2005) 1204*

5. *E. Glickman, L.Budic, M. Levenstein, N. Eliaz,* ***Interaction of liquid and solid gallium with thin silver films: synchronized spreading and penetration*** *,*
Acta Materialia , 59 (2011), 914-926

6. *E.Glickman* , **Dissolution Condensation Mechanism of SCC in Liquid Metals: Driving Force and Crack Kinetics**
Metallurgical and Materials Transactions A , v.42,#2(2011) 250

TIME to LME FAILURE under creep

$$t_f = \left(1 / \alpha\sigma^2\right) \times \left(K_c^2 / \sigma_y\right)$$

E. Glickman , A.Cherepanov et al.
, Soviet Phys. Journal., v.23 ,1980,364

Synergy between LME and Radiation Damages

- Radiation Embrittlement: $K_c \downarrow$
- Radiation Hardening: $\sigma_y \uparrow$

WHAT WE KNOW ABOUT LME

1.In BCC, FCC , HCP metals: poly- , single –crystalline and amorhphous

2.All types of phase diagrams “SM –LM“ , in particuilar without compounds

3. LME is crack kinetic problem : acceleration of subcritical crack velocity V(K) determines drop in durability

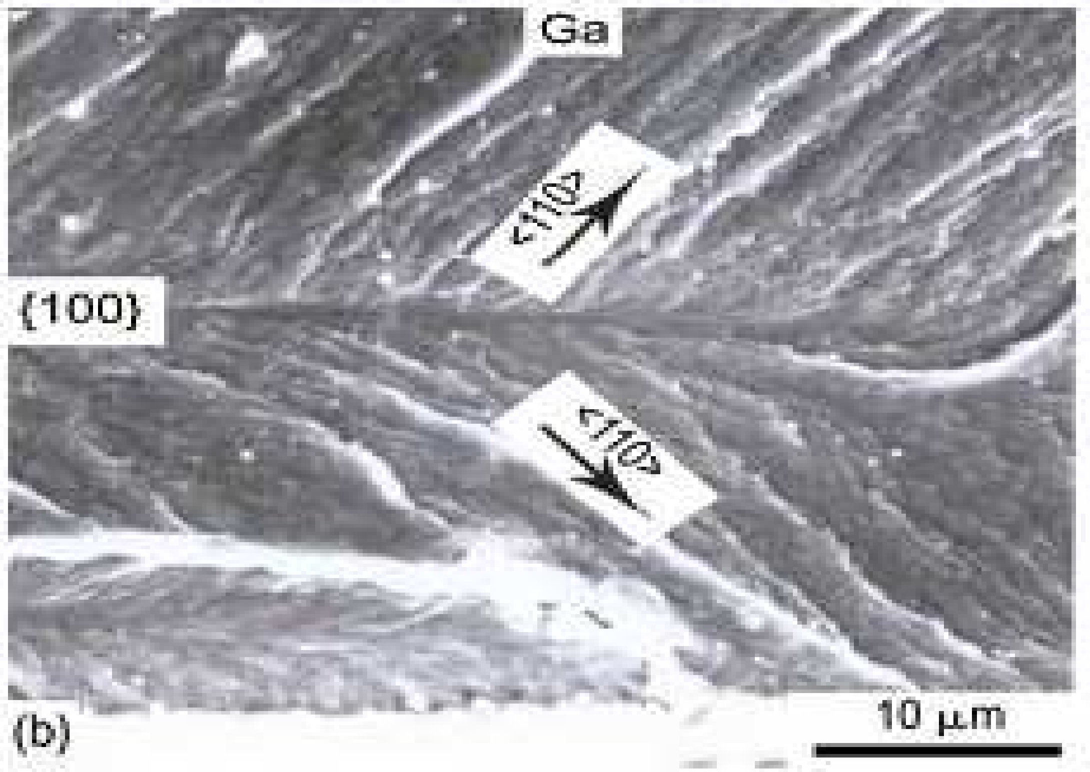
4.The toughness G_{IC} does not change

5. Three stage V(K) dependence is qualitatrively similar to that for SCC:
V_{II} can reach 10^{-1} m/s, the treshold toughness G_{TH} can be as small as ~0.1J/m^2

5. *V (K) increases* with T ; low activation energy H_A = (0.1... 0.4) eV

6. Large variety of fracture surfaces : from largely featureless to dimpled

Trans-granular fracture of β-brass single crystal in liquid Ga (S.Lynch)



CRACK KINETIKCS UNDER LME: 1

CHEMICAL POTENTIAL AT THE TIP

$$\mu_t = (\omega / h)(G - G_{TH})$$

h : width of the channel crack; ω : atomic volume; G_{TH} : empirical threshold

ENERGY RELEASE RATE

$$G \approx K^2 / E$$

E: Young modulus ; K : stress intensity factor

STRESS INTENSITY

$$K \approx \sigma L^{1/2}$$

σ: remote tensile stress; L: crack length

CRACK KINETIKCS UNDER LME (continued).2

SOLUTE CONCENTRATION IN LOCAL EQUILIBRIUM WITH THE TIP

$$\mathbf{C_t = C_\infty \exp \mu_t / kT}$$

C_∞ (T): solubility limit given by the phase diagram

CONCENTRATION GRADIENT IN LM

$$\mathbf{grad\ C \approx -(C_t - C_\infty) / \delta = -C_\infty (\exp \mu_t / kT - 1) / \delta}$$

CRACK OPENING DISPLACEMENT, COD

$$\boldsymbol{\delta = G / \sigma_P}$$

σ_P :yield stress in the plastic zone

REGIME I: $\mu_t / kT < 1$

"Plateau V_∞ after a threshold": ***explain behaviour of single-phase metals***

$$\ln V \approx \ln V_\infty - (K_{TH}/K)^2 \qquad (1)$$

$V_\infty = (D_L C_\infty C_j)(\sigma_p \omega / h kT) \neq f(K)$; **Activation Energy:** $H_I = H_{DL} + H_\infty + H_j$

REGIME II: $\ln(C_t^*/C_\infty) > \mu_t / kT > 1$

"Exponential growth with K^2"

$$\ln V = \ln(D_{0L}\sigma_p E/K^2) - (1/kT)[H - K^2(\omega/hE)][1-(K_{TH}/K)^2] \qquad (2)$$

Activation energy : $H_{II} = -\partial \ln V / \partial (1/T) = (H_I - \mu_t)$ can be even negative

REGIME III: $\mu_t / kT > [\ln(C_t^*/C_\infty) \approx -\ln C_\infty]$

"Saturation C_t (μ_t) at C_t^* causes the velocity saturation"

$$\ln V \leq \ln(C_j D_L \sigma_p E) - \ln K^2 \qquad (3)$$

A Popular Idea About Surface Energy Effect in Crystal Plasticity

Fracture and deformation create new surface; the smaller is γ, the easier it is to break/deform the solid. Wetting /Adsorption should thus always reduce the strength (The “Rehbinder effect”, from 1928 onward)

Skepticism About the Rehbinder Effect

For Metals

$(\Delta\gamma_{MAX} \sim 1\ J/m^2) << \gamma_{eff}$ for fracture & plastic flow

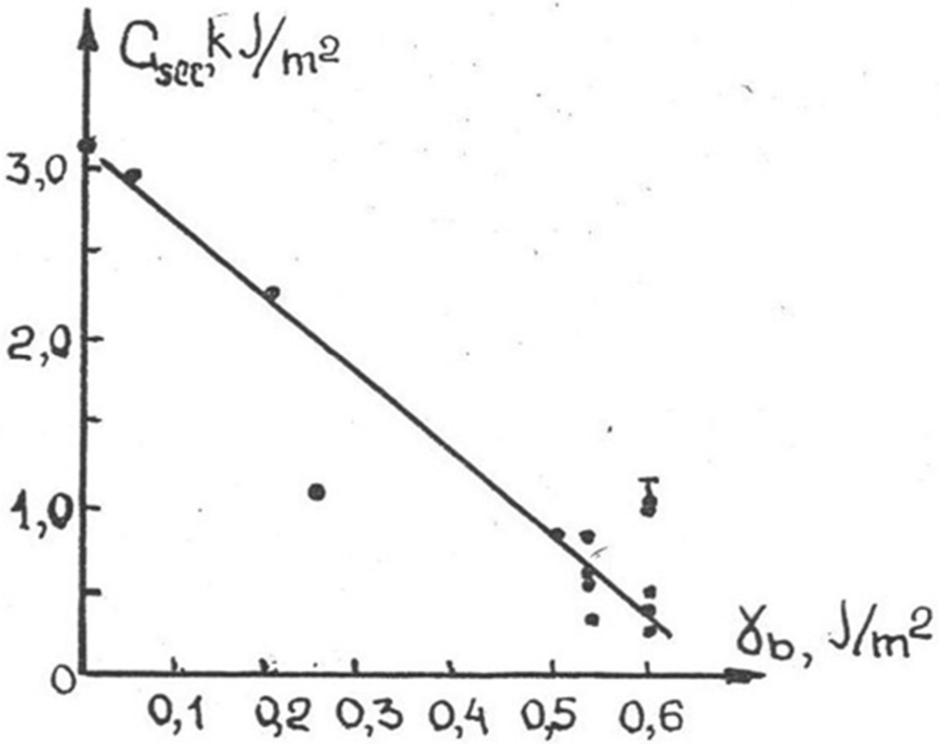
For Dielectrics:

- charge transfer to *near surface layers*
- no correlation between strength and $\Delta\gamma$ (*A. Westwood et al)*

LME of Al BiCRYSTALS by Ga:

Threshold G $_{TH}$ vs. GB ENERGY γ_b

J. Kargol et al, Met.Trans. A (1997) 8A, 271



Good agreement with experimental V(K) diagram [1] for Al-7075 exposed to Ga.

GALOP THEORY

$$V_\infty = C / (\Delta L^*)^2 \cdot [tg(\theta/2)]^3$$

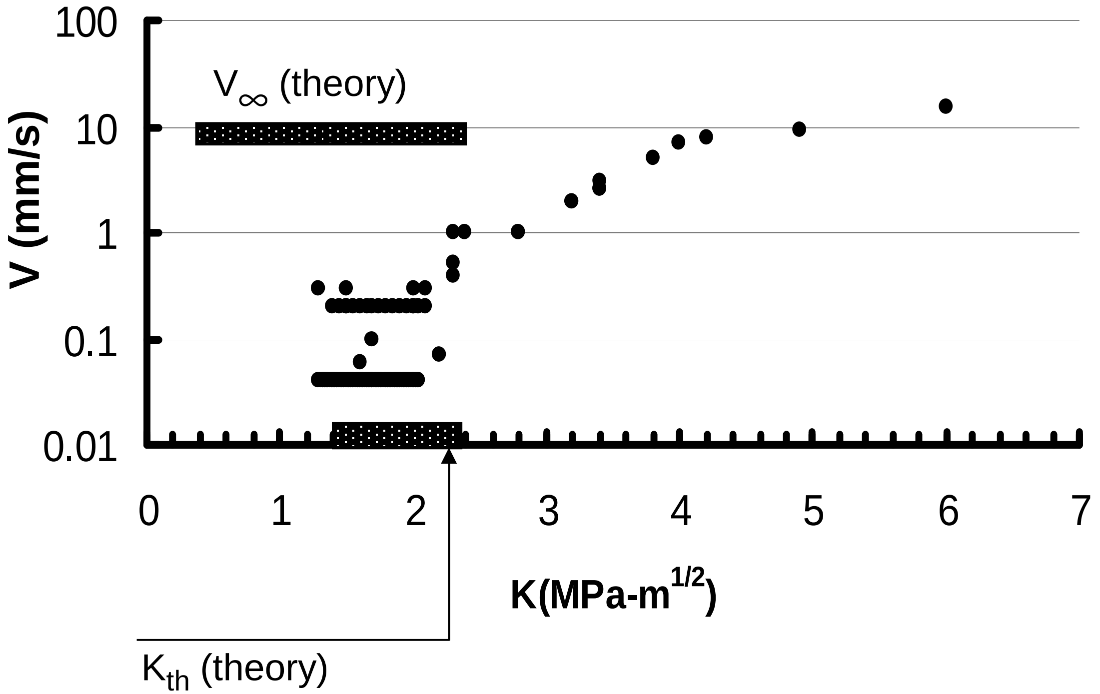
with $C = D_L\, C_{\infty L}\, \gamma_{SL} \Omega / kT$

$$K_{th}{}^2 = \varphi\, \Delta L^*\, tg(\theta/2) \cdot (\sigma_Y E)$$

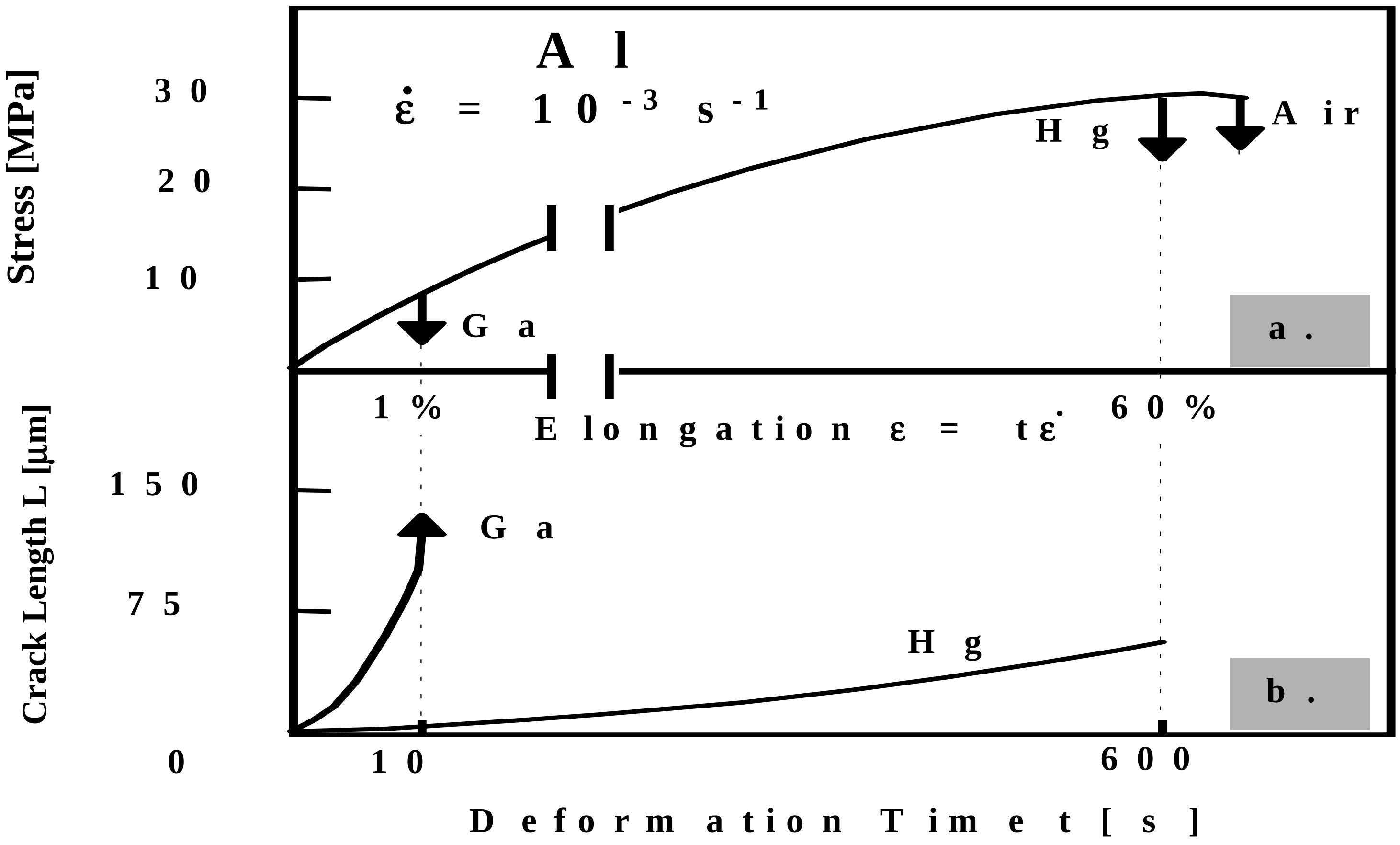
with $10<\varphi<50$

[1] D. Kolman and , R.Chavarria, 2001.

EXPERIMENT [1]



at (θ=20deg and $\Delta L^*=10^{-6}$ cm)
or (θ=60deg and $\Delta L^*=2 \cdot 10^{-7}$ cm) or
(θ=120deg and $\Delta L^*=4 \cdot 10^{-8}$ cm)



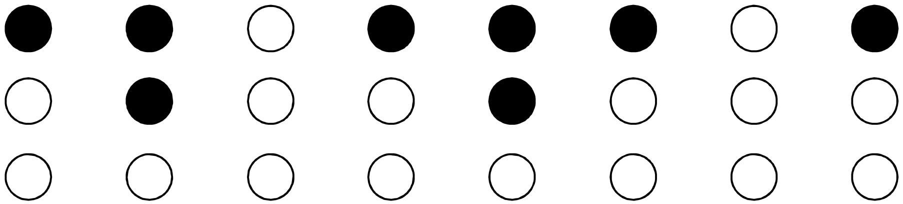
Subcritical Crack Kinetics determines strength and plasticity under LME tensile tests

Strength: R. Westwood et al. [1] ; Cracks : K. Saruchev et al [4]

LME as crack kinetic problem

Ad-metal Promoted Surface Diffusion (APSD)

● fast *[G. Rhead, F.Delamare, H. Bonzel]* ● operates in thin nm- channels



● adatom “B” (Bi)

○ substrate “A” (Cu)

Ad-metal enhanced diffusivity D_{AS} *(H. Bonzel)*

$$D_{AS}\left[cm^2/s\right]=10^{-2}\exp\left(-13T_{M3D}/RT\right)+740\exp\left(-30T_{M3D}/RT\right)$$

eutectic T from the phase diagram

LME-prone systems	**Cu-Bi, Al-Sn, Au-Pb**

$$D_{AS}\approx(10^{-5}-10^{-4})cm^2/s\ (\text{at } T/T_{M3D}\leq 1.25)$$

D_{AS} is larger than D_S and the liquid $D_L \approx 10^{-5} cm^2/s$

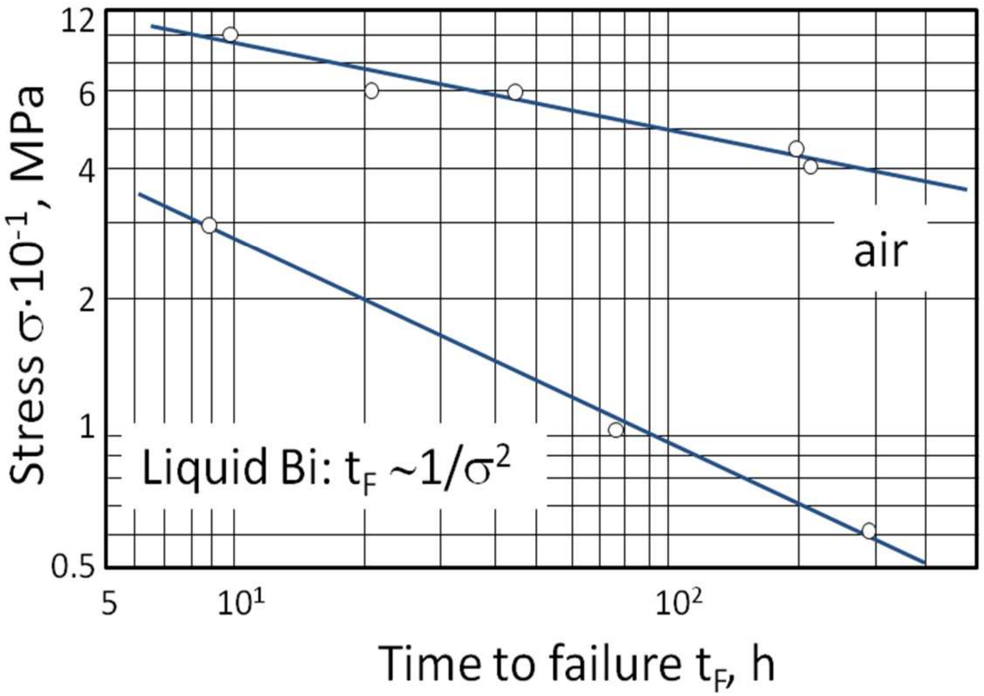
CONCLUSION	**APSD dominates in the channels and effectively couples LM diffusion**

Crack rate V_∞ is so fast that the only strategy to avoid LM failures is to use metals with $K_{th} > K$

K_{th} for fatigue cracks under LME may be several times smaller than the static K_{th} . [*R.E. Clegg and D.R. Jones*, *1994*]

Is K_{th} the true threshold or an apparent, kinetically affected threshold?

Stress dependence of time to failure at 350˚C
V. Nikitin (1967)



SURFACE ENERGY EFFECT IN PLASTICITY AND LME

1

The Rhebinder Effect (1928): Origin of Skepticism

2

Solid Metal/Liquid Metal Couples: Ideal Objects for Test

- LMs are very strong surfactants towards solid ones
- No sub-surface effects like in dielectrics
- Massive dissolution can be easily prevented

3

Unique couple: Solid Cu / Liquid Bi_XPb_{1-x}

•Surface energy isotherm $\gamma_{SL}=f(X)$ is known, ***Fig…***

•Bi and Pb form simple eutectic phase diagram with *Cu* and show unlimited mutual solubility above 330 C .

•Strong LME was reported : three major forms, ***Fig…***

4

Subcritical crack kinetics:

- L(t) in Bi vs. Ar, ***Fig…***
- SEM /TEM of the crack tip
- Activation energy
- Acoustic emission
- Exponentially strong effect of γ_{SL} on crack, void & creep rates, ***Fig…***

5

Dissolution- Condensation Mechanism by Robertson –Glickman (Fig…)

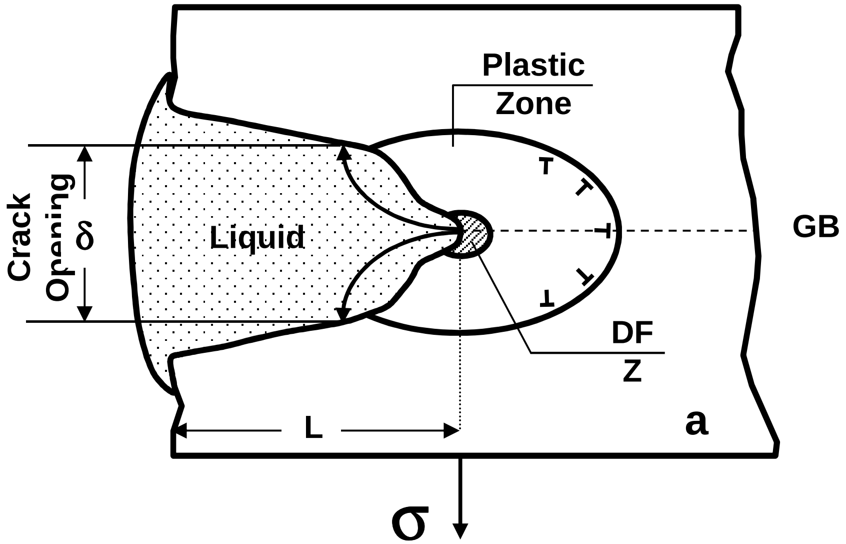
- Detachment at the Tip - Fast diffusion through liquid--Attachment at the Crack walls
- Solid-liquid interface becomes atomically rough with strong reduction in γ_{SL}

6

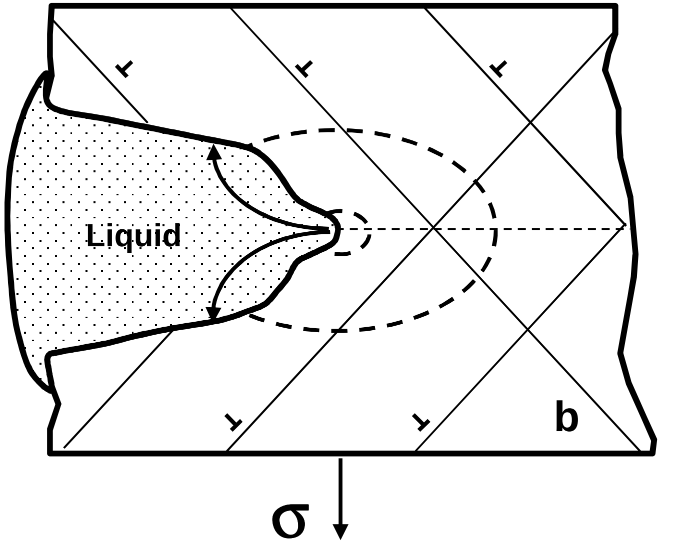
Summary

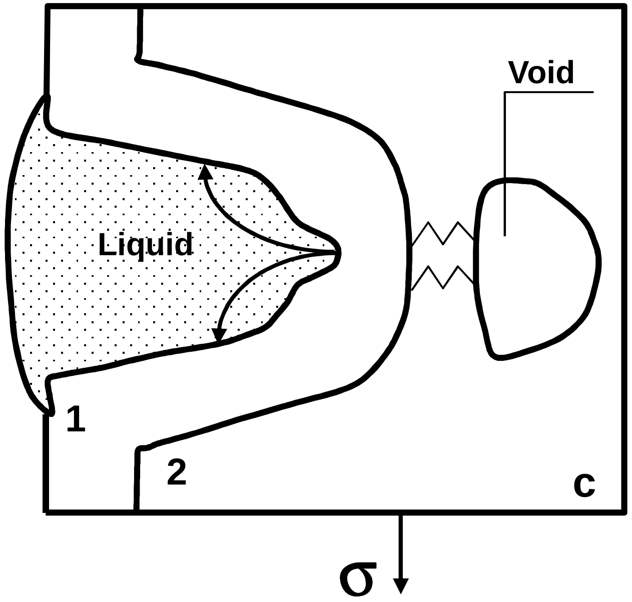
Shielded Crack is arrested when

$$K_{shield} \approx 0.1\{G_M\, b^{½}\} < [\,E\,(\gamma_{SL} - 0.5\gamma_{GB})]^{½}$$



- De-shielding by <u>general yielding</u> allows crack extension at $G_{th} \sim \gamma_{SL.}$
- Crack velocity for DCM: $V_{DCM} \leq D_L C_{\infty L} / \delta$





- Deshielding by <u>formation of voids / cracks</u> in the plastic zone requires $G_{th} >> \gamma_{SL}$

- Crack velocity for combined kinetic mechanism (DCM + necking):

$$V' =(\,A \cdot V_{DCM}\,) \sim 10^3 \cdot V_{DCM}$$

$$A = 8 / \{\varepsilon\, [(\theta/\sigma)-1]\}$$

[J.M. Kraft & M. Mullherin, 1969.]

θ is strain hardening coefficient

DISSSOLUTION - CONDENSATION MECHANISM OF LME:

Roberson – Glickman Model

W. M. Robertson (1966)

* Sharp crack → large local stress → increase in the chemical potential μ_{tip} of SM at the tip
*Fast out-of-the tip diffusion of SM atoms through LM
*Condensation at the crack banks

E. Glickman et al (1976 , 2003, 2011)

* Blunted crack + narrow channel ahead it ; the channel opening h<<COD
*Small h provides large μ_{tip} ~(G/ h) and favors thus fast crack extension
*Periodic re-blunting from h to COD after crack increment ΔL=(2…3)COD

+

* Wetting induced atomic roughening → accelerates detachment / attachment processes at the solid /liquid interface → accelerate cracks , creep, and vacancy voiding near the interface

Threshold $G_{TH} = 2\gamma_{eff}$ for LME in several single-phase metals is comparable to $2\gamma_{SL}$ for the solid/liquid interfaces. In aging alloys $G_{TH} >> \gamma_{SL}$ and varies over 3 decades . **We suppose shielding / precipitate bridging.**

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